

Supporting Information

D^MP DAB–Pd–MAH: A Versatile Pd(o) Source for Precatalyst Formation, Reaction Screening, and Preparative-Scale Synthesis

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I: General Considerations

Materials. All solvents and common organic reagents were purchased from commercial suppliers and used without further purification. All palladium sources (except $\text{Pd}_2\text{dba}_3 \bullet \text{CHCl}_3$) were purchased from Strem Chemicals and used as received. $\text{Pd}_2\text{dba}_3 \bullet \text{CHCl}_3$ was prepared according to the method of Zalesskiy and Ananikov.¹ *N,N'*-bis(2,6-dimethylphenyl)ethan-1,2-diimine was prepared using a reported procedure.² $t\text{BuDAB-Pd-MAH}$ was prepared using a reported procedure.³ All phosphine ligands were purchased from Strem Chemicals and used as received. Anhydrous solvents (SureSeal) were purchased from MilliporeSigma and used as received.

Techniques. All air-free manipulations were performed under a dry nitrogen atmosphere using an MBraun glovebox. High-throughput experimentation was performed using 1 mL capacity glass shell vials in sealable aluminum reaction blocks purchased from Analytical Sales. Heating/stirring was achieved using rare-earth magnetic tumble stirrers acquired from V&P Scientific.

Analysis and Spectroscopy. All NMR spectra were acquired on either a Bruker AVANCE 300 MHz spectrometer or a Bruker AVANCE Neo 500 MHz spectrometer. All ^1H and ^{13}C NMR chemical shifts are calibrated to residual protio-solvents and all ^{31}P NMR chemical shifts are calibrated to external standards. All NMR spectroscopic data is processed using Bruker TopSpin 4.07.

UPLC analysis was performed using a Shimadzu Nexera X2 instrument consisting of an autosampler, binary pumps, degassing unit, column oven with a diode-array UV/Vis detector. A Raptor ARC-18 column (100×2.1 mm, particle size $1.8 \mu\text{m}$) and a Waters CORTECS® UPLC® T3 column (2.1×30 mm, particle size $1.6 \mu\text{m}$) were used. The eluent used is the mixture of two mobile phases. Water with 0.05% trifluoroacetic acid (TFA) was set to be the mobile phase A, and acetonitrile with 0.05% TFA was set to be the mobile phase B. The gradient profiles, flow rates and injection volumes used for analysis are shown in Section III. The assignments to the key peaks are based on the retention times of isolated compounds and starting materials using the same separation method. All solvents used were HPLC grade.

LCMS analysis was performed using a Waters Acquity class H UPLC system which consists of a quaternary pump, a Sampler Manager-Flow Through Needle, columns selection module with an oven compartment, a photodiode array detector, and a QDa Mass Spectrometer. An ACQUITY UPLC® BEH C18 column (2.1×50 mm, particle size $1.7 \mu\text{m}$) was used for the analysis of C-O coupling. The solvent mixture consists of solvent A which was water with 0.4% formic acid (FA) and solvent B was set to be acetonitrile with 0.4% FA. The detailed separation methods are also included in Section III. The assignments to the key peaks are also based on the retention times of the isolated product and starting materials using the same separation method. Masslynx was used to process the data. All solvents used were LC-MS grade.

High-resolution electrospray ionization mass spectrometric analysis was performed using a Thermo Scientific Ultimate 3000 ESI-Orbitrap Exactive Plus.

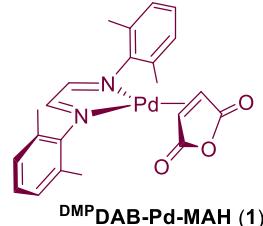
Details of X-ray crystallography studies are given in Section V.

II: Synthesis and Characterization of Palladium Complexes

Synthesis of ^{DMP}DAB–Pd–MAH (1)

Both of these procedures are carried out under ambient atmosphere.

From Pd₂dba₃•CHCl₃: A 250 mL round bottom flask containing a stirbar was charged with Pd₂dba₃•CHCl₃ (251.5 mg, 0.243 mmol), N,N'-bis(2,6-dimethylphenyl)ethan-1,2-diimine (134.4 mg, 0.510 mmol, 2.1 equiv), and maleic anhydride (51.4 mg, 0.522 mmol, 2.15 equiv). Acetone (45 mL) was added to dissolve/suspend the components. The reaction mixture was stirred at room temperature for three hours, producing a dark purple/red homogeneous solution. The reaction solution was concentrated under vacuum to a volume of approximately 2 mL. TBME (40 mL) was added and the solution was stirred for 15 minutes, producing a purple/red slurry. After the solid settled, the TBME was decanted, leaving a purple/red solid. The solid was dissolved in a minimum of acetone and filtered through Celite to remove palladium black. The Celite bed was thoroughly rinsed with acetone until the rinsings were colourless, and the combined filtrate was evaporated under vacuum. The resulting purple/red solid was washed with TBME (3 x 10 mL) and dried under vacuum to give compound **1** (187 mg, 82% yield).



DMPDAB-Pd-MAH (1)

From Pd(OAc)₂: A 1 L round bottom flask containing a stirbar was charged with dibenzylideneacetone (dba, 6.26 g, 26.7 mmol, 2 equiv) and sodium acetate (10.96 g, 133.6 mmol, 10 equiv). Methanol (250 mL) was added and the mixture stirred to ensure dissolution of the dba. With stirring, solid Pd(OAc)₂ (3.00 g, 13.4 mmol) was added through a powder funnel, which was rinsed with methanol (50 mL) to ensure quantitative transfer. The flask was immersed in an oil bath kept at 40–45 °C. The reaction mixture was stirred vigorously at this temperature for 3 hours. The flask was then cooled to room temperature. The resulting dark slurry was filtered through filter paper in a Buchner funnel to collect the crude “Pd(dba)₂” solid. The solid was washed successively with methanol (3 x 30 mL), water (3 x 30 mL), and acetone (2 x 10 mL). This solid was then transferred to a 1 L round bottom flask containing a stir bar, and slurried in acetone (300 mL). Solid N,N'-bis(2,6-dimethylphenyl)ethan-1,2-diimine (3.71 g, 14.0 mmol, 1.05 equiv) and maleic anhydride (1.38 g, 14.0 mmol, 1.05 equiv) were added through a powder funnel, which was rinsed with acetone (100 mL) to ensure quantitative transfer. The reaction mixture was stirred at room temperature for 3 hours. The dark red solution was filtered through a bed of Celite using a medium porosity frit to remove palladium black. The Celite bed was thoroughly rinsed with acetone until the rinsings were colourless, and the combined filtrate was evaporated under vacuum. TBME (100 mL) was added and the solid triturated in the flask. The purple/red solid was collected by suction filtration, and the filter cake was washed with TBME (6 x 10 mL, until rinsings are colourless) to completely remove dba. The solid was dried under vacuum to give compound **1** (3.60 g, 57% yield from Pd(OAc)₂). See Figure S1 for images from key stages of the synthesis.

¹H NMR: (300 MHz; *d*₆-acetone) δ 2.17 (s, 12H, 4 x Ar–CH₃), 3.44 (s, 2H, –CH=CH–), 6.99 (m, 6H, 6 x Ar–H), 8.42 (s, 2H, 2 x –CH=NAr). ¹³C{¹H} NMR: (125 MHz; *d*₆-acetone) 17.3 (4 x Ar–CH₃), 42.1 (–CH=CH–), 126.2 (Ar), 128.2 (Ar), 149.0 (Ar), 165.2 (–N=C–C=N–), 171.0 (2 x C=O). HRMS (ESI) of [C₂₂H₂₂N₂O₃Pd•Na]⁺ (major isotopomer, sodium adduct): 491.05575 (calc'd); 491.05511 (found). Elemental analysis (CHN) of C₂₂H₂₂N₂O₃Pd: 56.36, 4.73, 5.98 (calc'd); 56.33, 4.79, 5.84 (actual). Elemental analysis performed on batch of compound prepared from Pd(OAc)₂ (synthesis shown in Fig. S1). Sample stored in air for >7 months prior to analysis.

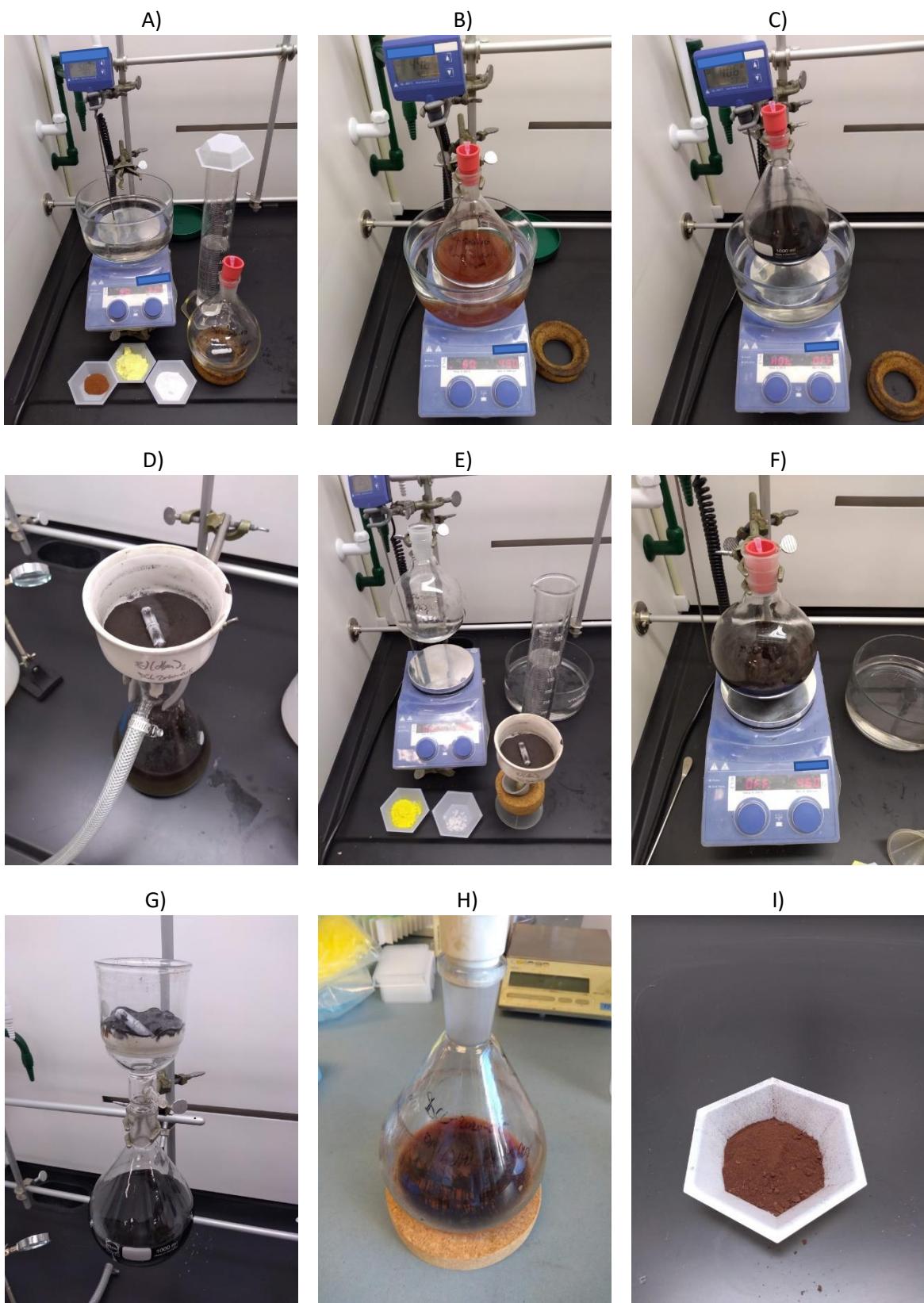


Figure S1. Synthesis of DAB–Pd–MAH (**1**) from 3.00 g Pd(OAc)₂. A) Materials for “Pd(dba)₂” synthesis. B) Initial reaction mixture. C) Reaction mixture after heating to 40–45 °C for 3 h. D) Isolation of crude “Pd(dba)₂”. E) Materials for synthesis of **1**. F) Initial reaction mixture. G) Celite filtration to remove Pd black. H) TBME reslurry/trituration. I) Isolated solid.

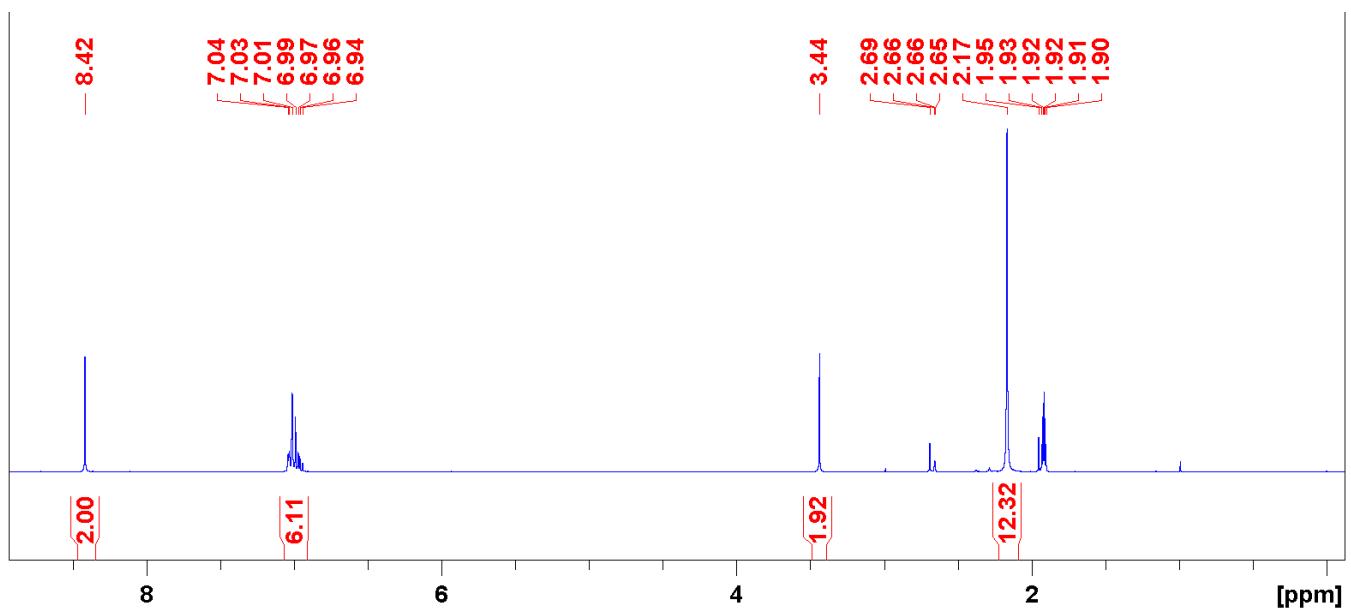


Figure S2. ^1H NMR spectrum (300 MHz; d_6 -acetone) of **1**. Quintet at 1.92 ppm is d_5 -acetone; singlet at 1.95 ppm is acetone; 1:1:1 triplet at 2.65 ppm is HDO; singlet at 2.69 ppm is H_2O .

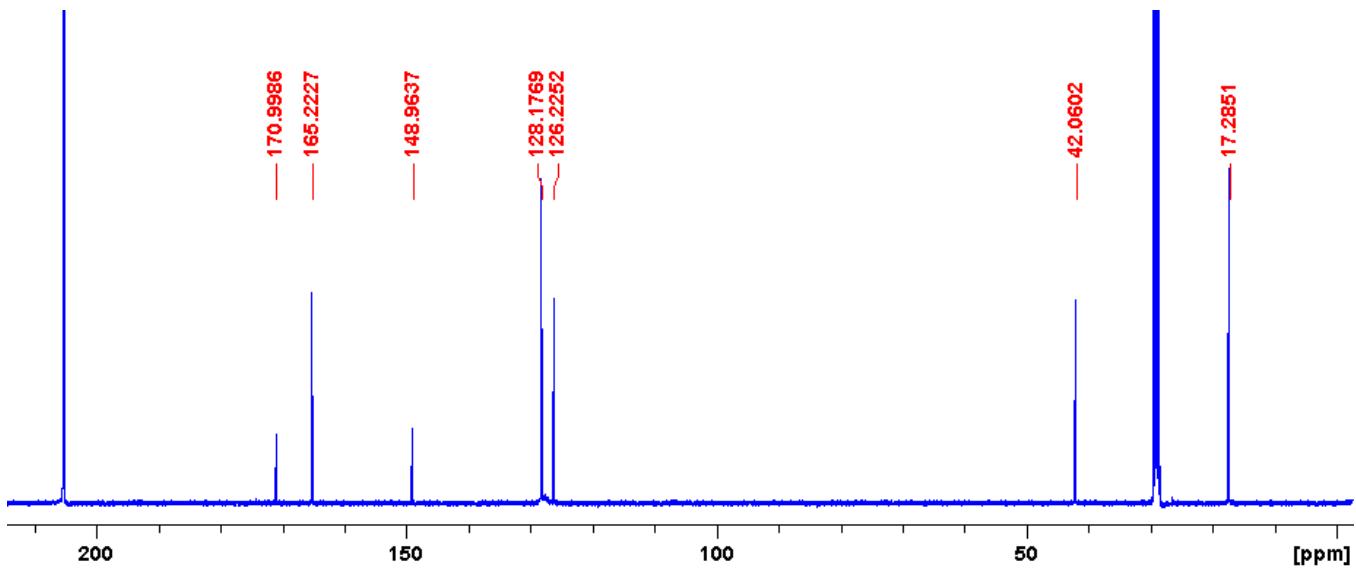


Figure S3. ^{13}C NMR spectrum (125 MHz; d_6 -acetone) of **1**.

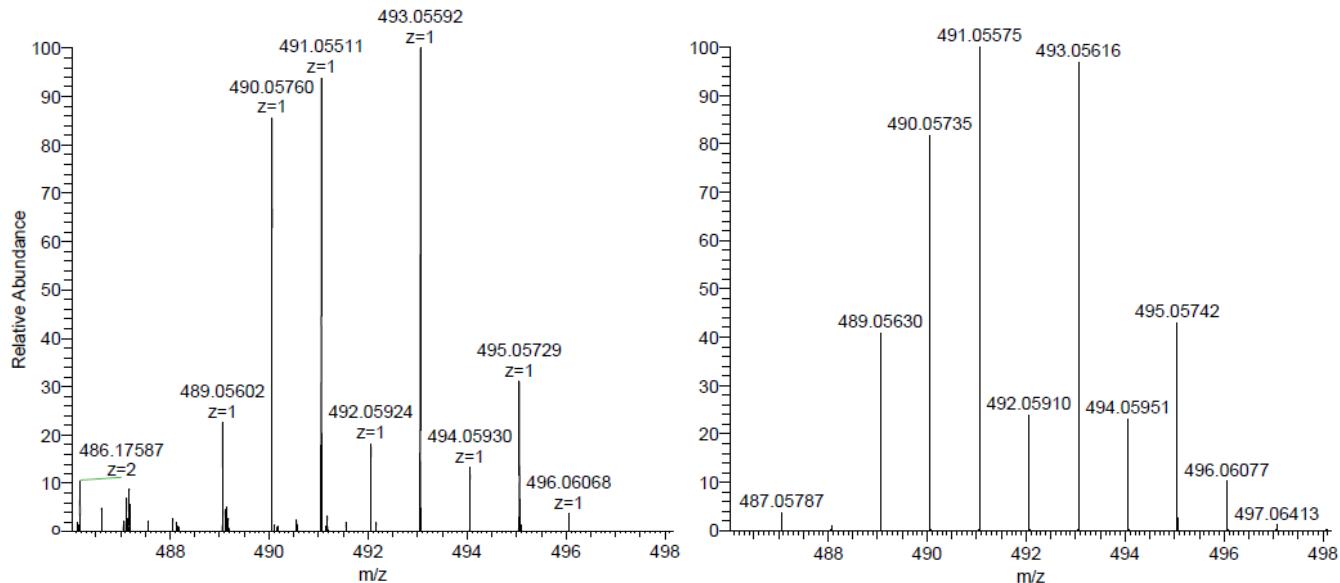


Figure S4. *Left:* Experimental HRMS-ESI spectrum of $[1 \bullet \text{Na}]^+$. *Right:* Calculated HRMS isotope pattern for $[1 \bullet \text{Na}]^+$.

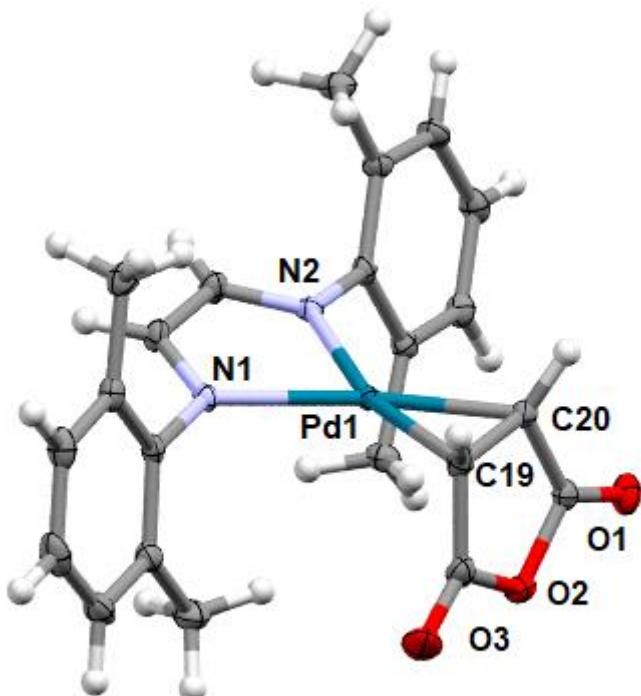


Figure S5. Solid-state molecular structure of complex 1. Thermal ellipsoids plotted at 50% probability for non-H atoms; H-atoms shown as uniformly-sized white spheres for clarity. Selected bond lengths (Å) and angles (°): Pd1–N1: 2.1342(11); Pd1–N2: 2.1520(11); Pd1–C19: 2.0556(14); Pd1–C20: 2.0868(13); C19–C20: 1.4315(18); N1–Pd1–N2: 76.30(4); C19–Pd1–C20: 40.42(5); N1–Pd1–C19: 117.93(5); N2–Pd1–C20: 124.67(5).

Solution Stability of ^{DMP}DAB–Pd–MAH (1)

In air, complex **1** (12.0 mg, 0.0256 mmol) was dissolved in six different deuterated solvents (CDCl_3 , CD_2Cl_2 , d_6 -acetone, CD_3CN , d_6 -DMSO, and d_8 -THF; 0.6 mL each) to generate solutions of 20 mg **1** / 1 mL solvent. Complex **1** is not soluble in d_6 -DMSO, so this solvent was omitted from the stability analysis. 1,3,5-Trimethoxybenzene (~3 mg) was added to each solution as an internal standard. Initial ¹H NMR spectra were obtained for each solution after 30 minutes (300 MHz), and the peak area ratio for the imine C–H signal (8.43 ppm in d_6 -acetone) and the internal standard Ar–H signal was recorded. Subsequent ¹H NMR spectra were obtained at 2, 6, 18, 24, 30, 42, and 48 hours; Figure S6 contains representative stack plots for spectra obtained in CDCl_3 (top) and d_6 -THF (bottom). The peak area ratio for the imine C–H signal and the internal standard Ar–H signal for each spectrum was divided by the initial ratio to generate the normalized concentration data in Table S1. For CDCl_3 and CD_3CN , a palladium mirror was clearly visible on the inside wall of the NMR tubes after 18 hours, whereas the NMR tubes containing the CD_2Cl_2 , d_6 -acetone, and d_8 -THF solutions remained mirror-free over 48 hours.

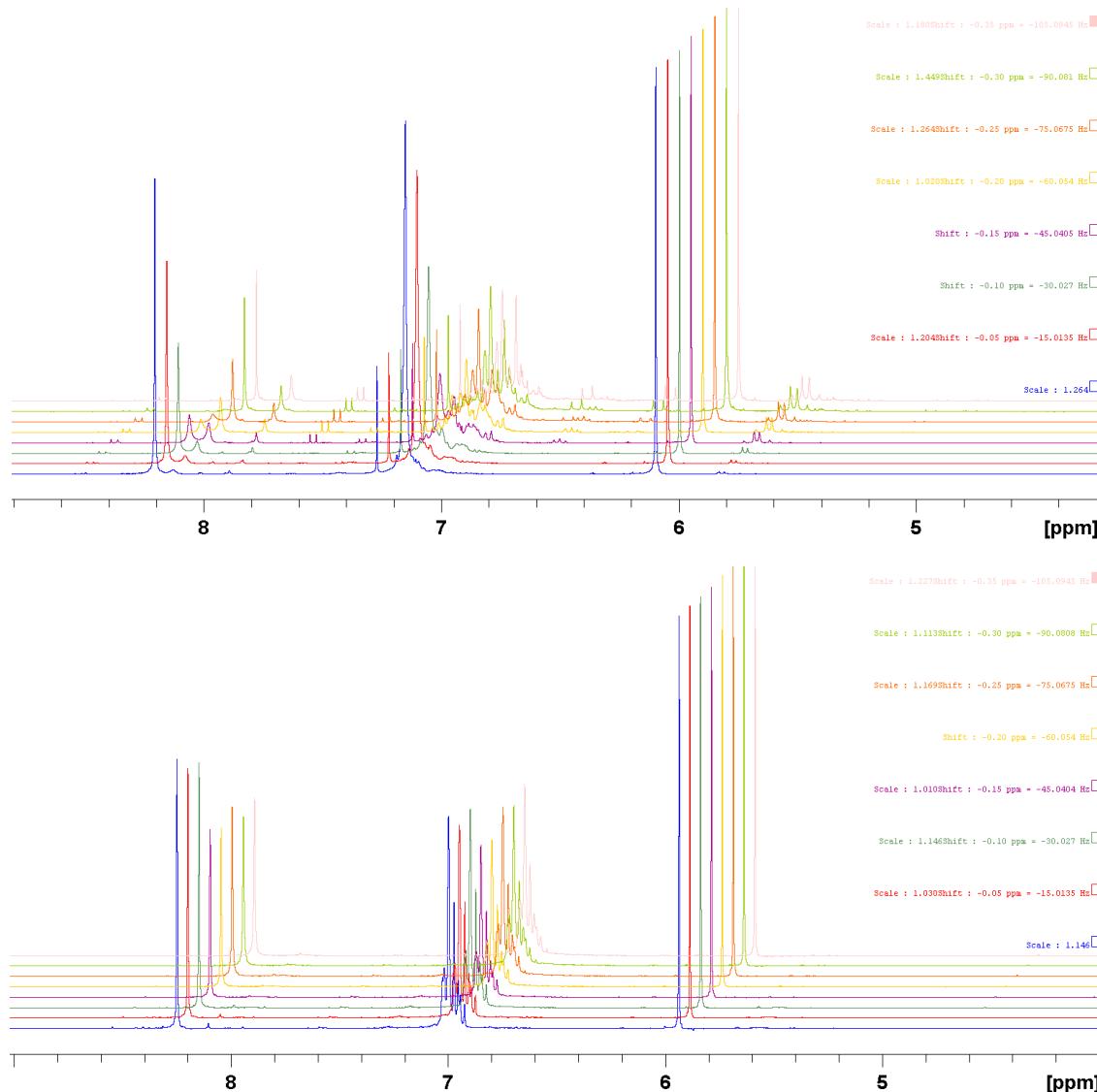


Figure S6. ¹H NMR spectra (300 MHz) stack plots for solution stability of **1** in CDCl_3 (top) and d_6 -THF (bottom) with time increasing from front (30 min) to back (48 h). Key peaks are the imine C–H signal (~8.2 ppm), the DMP aromatic signals (~7 ppm), and the Ar–H signal for 1,3,5-trimethoxybenzene internal standard (~6 ppm).

Table S1. Normalized [1] (starting from an initial concentration of 20 mg / mL) for solutions using five different deuterated solvents over 48 hours to assess stability.

Time (h)	[1]/[1] _{30min}				
	CDCl ₃	CD ₂ Cl ₂	d ₆ -acetone	CD ₃ CN	d ₆ -THF
0.5	1.00	1.00	1.00	1.00	1.00
2	0.93	0.98	0.99	0.97	0.99
6	0.78	0.97	1.00	0.81	0.97
18	0.45	0.94	0.94	0.48	0.91
24	0.24	0.92	0.93	0.30	0.89
30	0.12	0.91	0.93	0.20	0.91
42	n/d	0.86	0.87	n/d	0.93
48	n/d	0.84	0.85	n/d	0.92

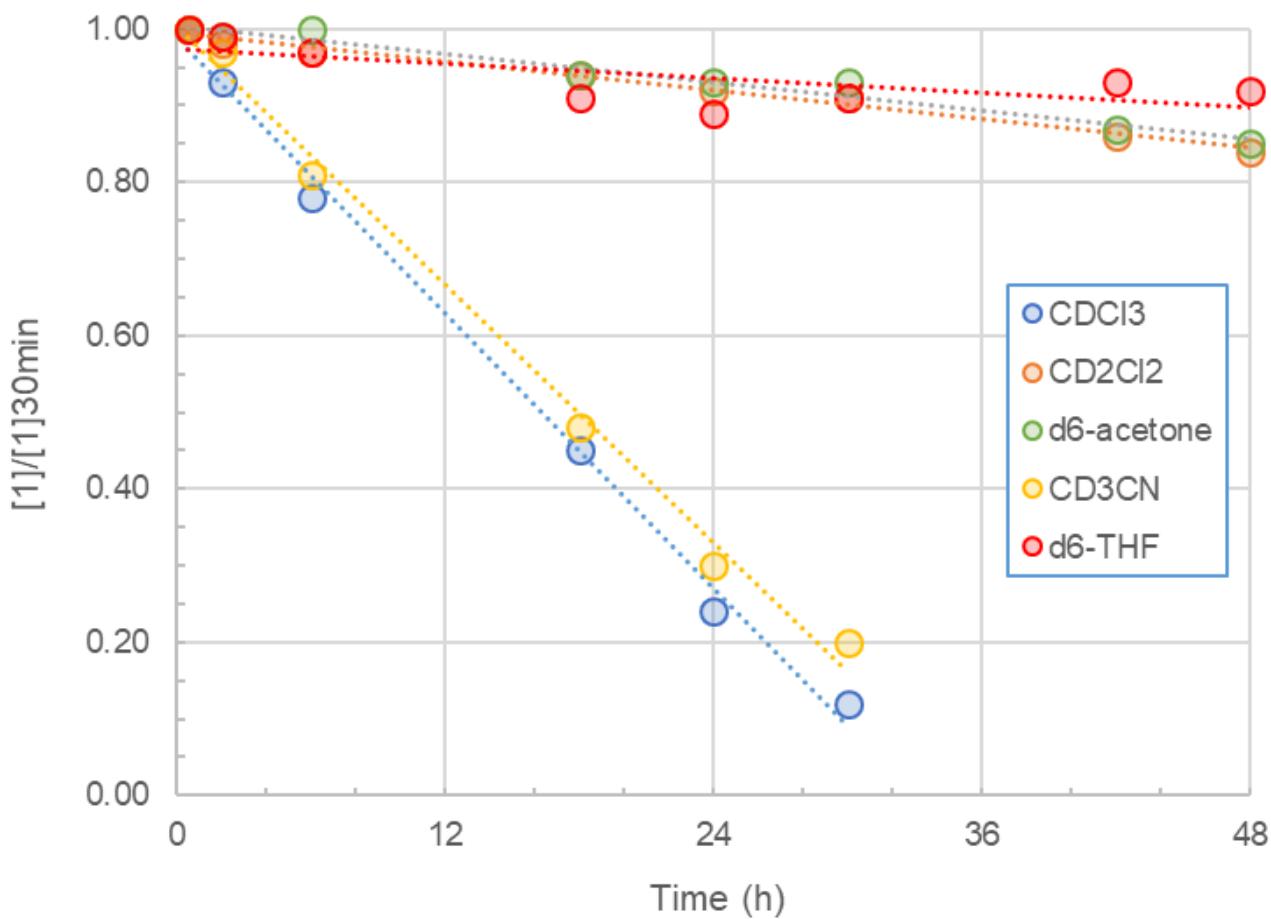


Figure S7. Plot of normalized [1] (starting from an initial concentration of 20 mg / mL) for five different deuterated solvents over 48 hours at room temperature under air.

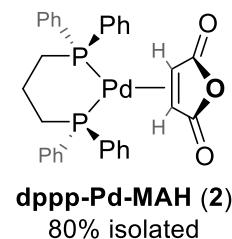
Synthesis of [phosphine]–Pd–MAH complexes

Unless otherwise noted, the following general procedure was used to prepare all of the following phosphine–Pd–MAH complexes. Starting materials were handled and weighed under inert dinitrogen atmosphere in the glovebox (due to oxygen-sensitivity of the phosphines). A 20 mL vial or 50 mL round-bottom flask was charged with complex **1** (100.0 mg, 0.2133 mmol), the corresponding phosphine ligand (1.05 equiv, 0.2240 mmol), and a cross-shaped magnetic stirbar. Anhydrous, degassed THF (5-15 mL) was added, and the reaction mixture stirred for 1-2 hours. During this time, the solution changes colour from an initial dark red/purple to yellow/orange; the exact final colour and the rate of colour change depends on the phosphine used. Note: after the 1-2 hours stirring, the solution can be opened to ambient atmosphere if desired.

The solvent was then removed *in vacuo* to give a yellow to orange residue. This residue was triturated with hexanes or diethyl ether (2-4 mL), followed by decantation of the liquid phase (with or without centrifugation as required). This trituration/decantation process was repeated 2-5 more times to remove the ^{DMP}DAB byproduct, as well as any excess phosphine. The solid was then dried *in vacuo* to give the product.

dppp–Pd–MAH (**2**)

Previously reported compound⁴ prepared according to the general procedure using **1** (123.0 mg, 0.2623 mmol), dppp (113.6 mg, 0.2755 mmol), and THF (5 mL). Trituration/decantation 3 x with diethyl ether (4 mL). Tan solid: 130.0 mg (80%). ¹H NMR: (300 MHz; CDCl₃) δ 1.58-1.75 (m, 1H, dppp tether), 2.25-2.34 (m, 3H, dppp-tether), 2.61-2.73 (m, 2H, dppp tether), 4.07 (m, 2H, –CH=CH–), 7.32-7.46 (m, 16H, Ar–H), 7.57-7.83 (m, 4H, Ar–H); ¹³C{¹H} NMR: (125 MHz; CDCl₃) δ 18.9 (t, *J* = 3.8 Hz), 27.5 (m), 52.7 (m), 128.8 (t, *J* = 5.0 Hz), 128.9 (t, *J* = 5.0 Hz), 130.0, 130.6, 131.7 (t, *J* = 6.3 Hz), 132.7 (m), 133.2 (t, *J* = 7.5 Hz), 136.1 (m), 171.6; ³¹P{¹H} NMR: (121 MHz; CDCl₃) δ 10.2. HRMS (ESI) of [C₃₁H₂₈O₃P₂Pd•Na]⁺ (major isotopomer, sodium adduct): 639.04407 (calc'd); 639.04408 (found). Elemental analysis (CH) of C₃₁H₂₈O₃P₂Pd: 60.35, 4.57 (calc'd); 60.33, 4.61 (actual).



See Figures S8-S13 for characterization data.

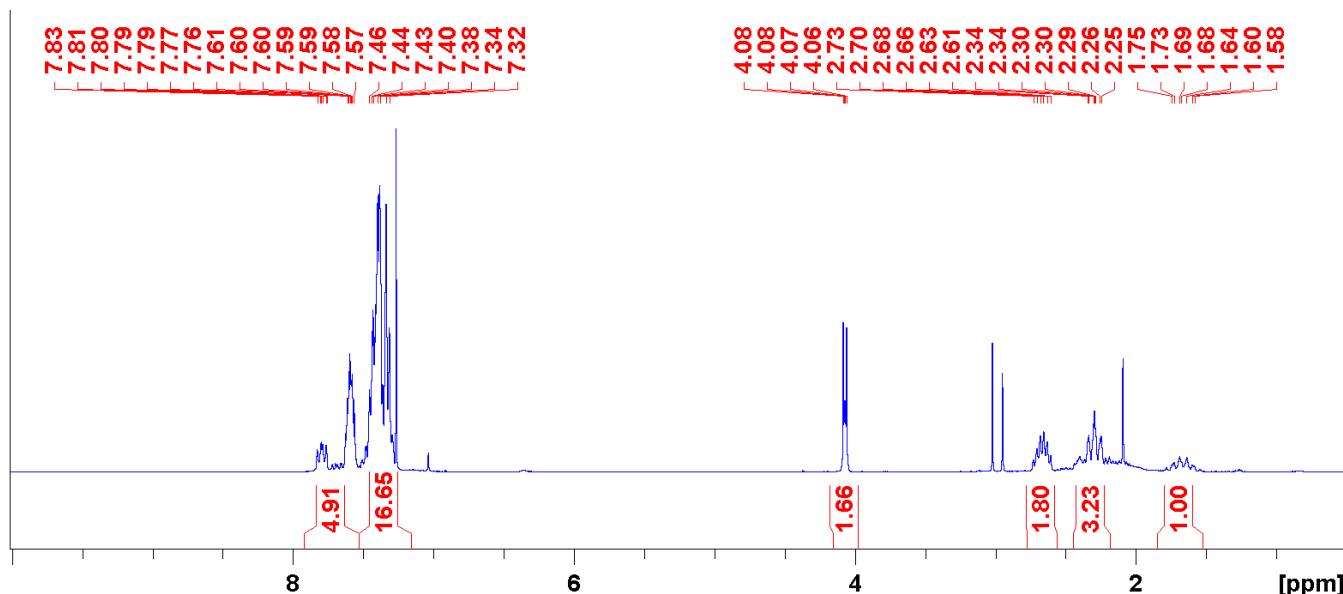


Figure S8. ¹H NMR spectrum (300 MHz; CDCl₃) of **2**.

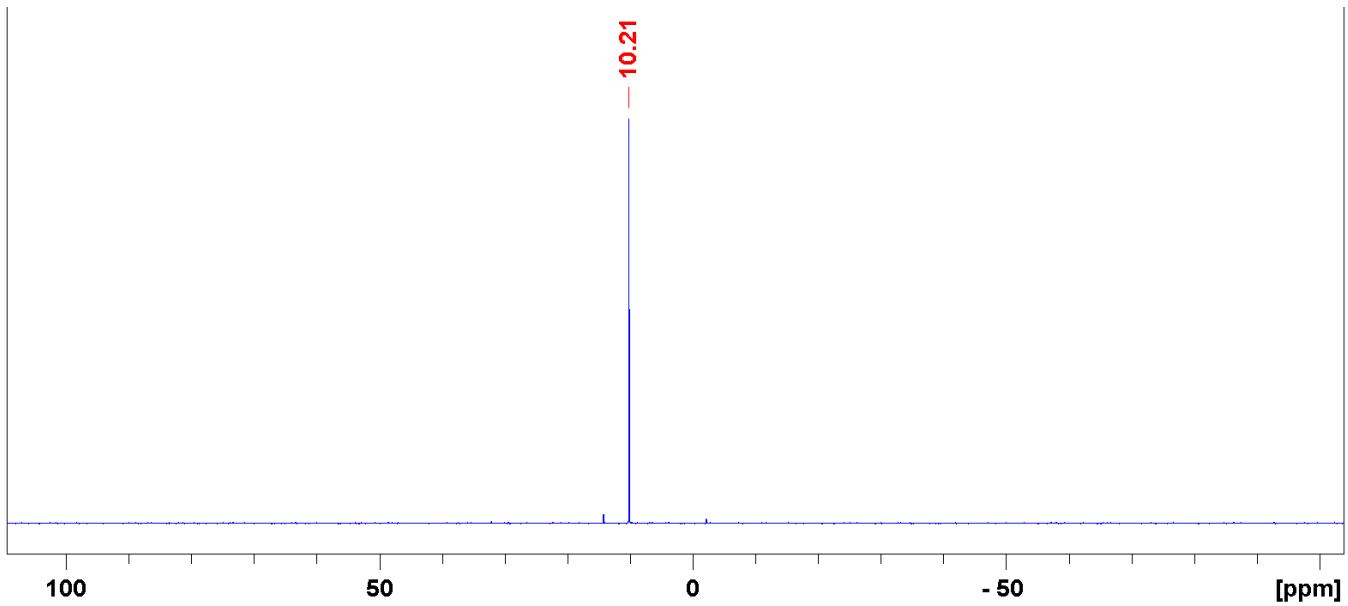


Figure S9. ^{31}P NMR spectrum (121 MHz; CDCl_3) of **2**.

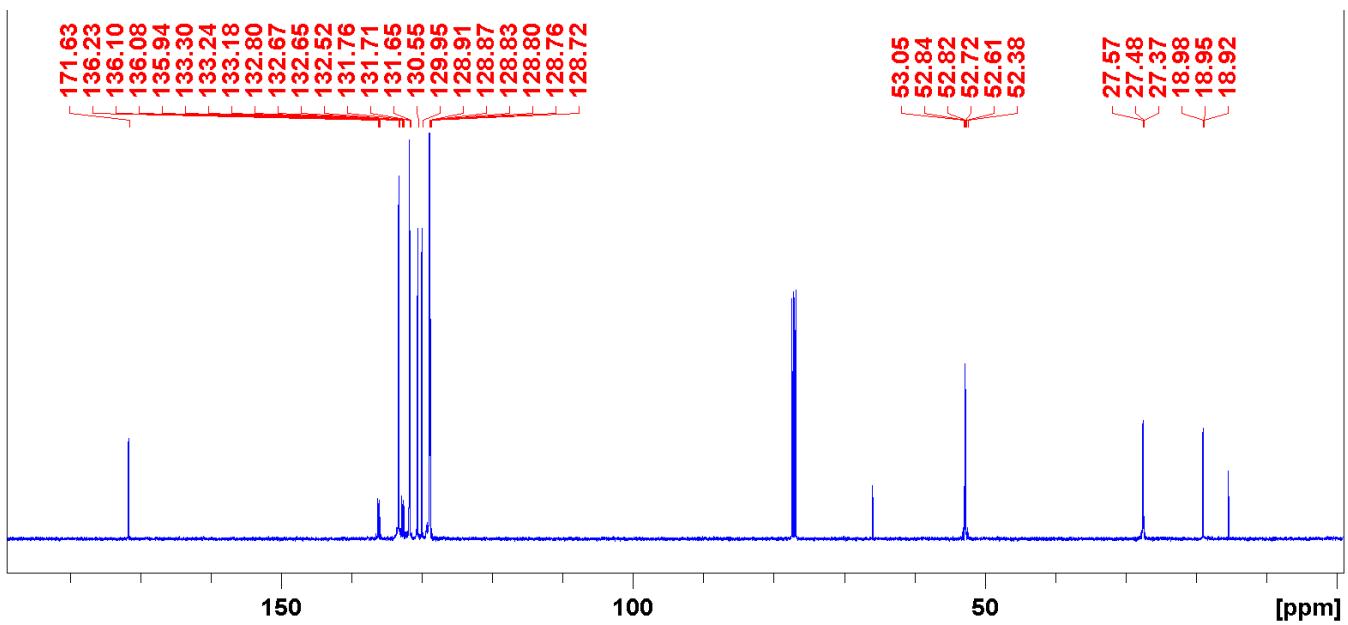


Figure S10. ^{13}C NMR spectrum (125 MHz; CDCl_3) of **2**. Full spectrum window.

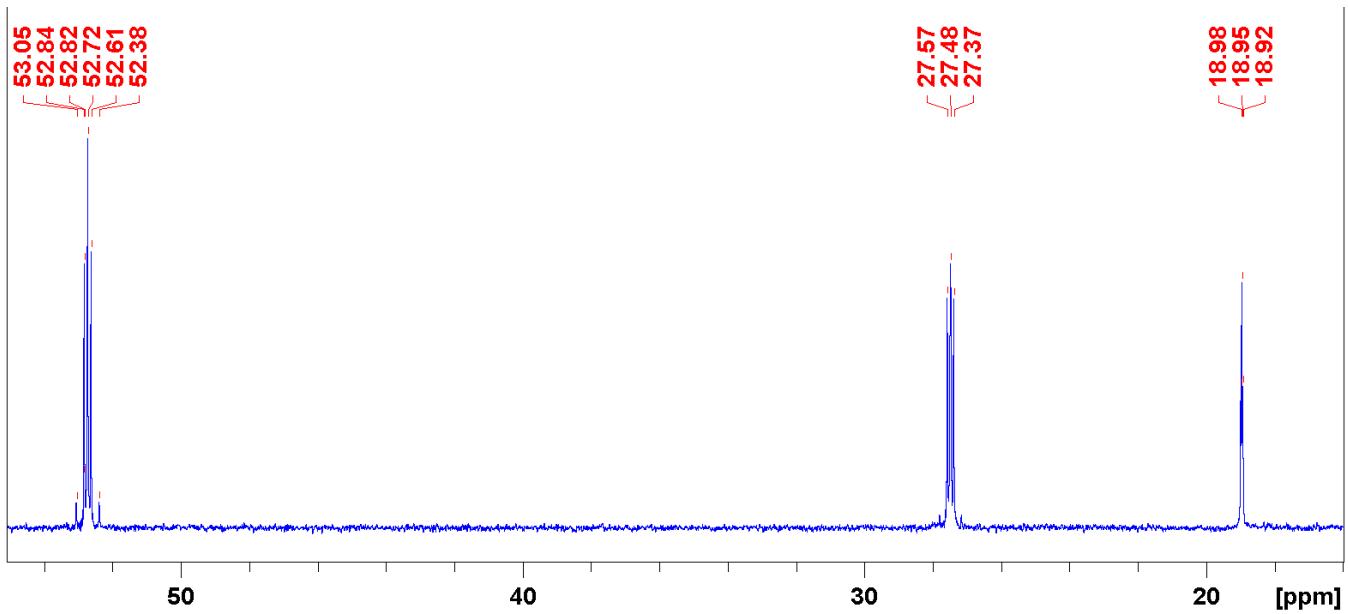


Figure S11. ¹³C NMR spectrum (125 MHz; CDCl₃) of **2**. Expansion of aliphatic carbon region.

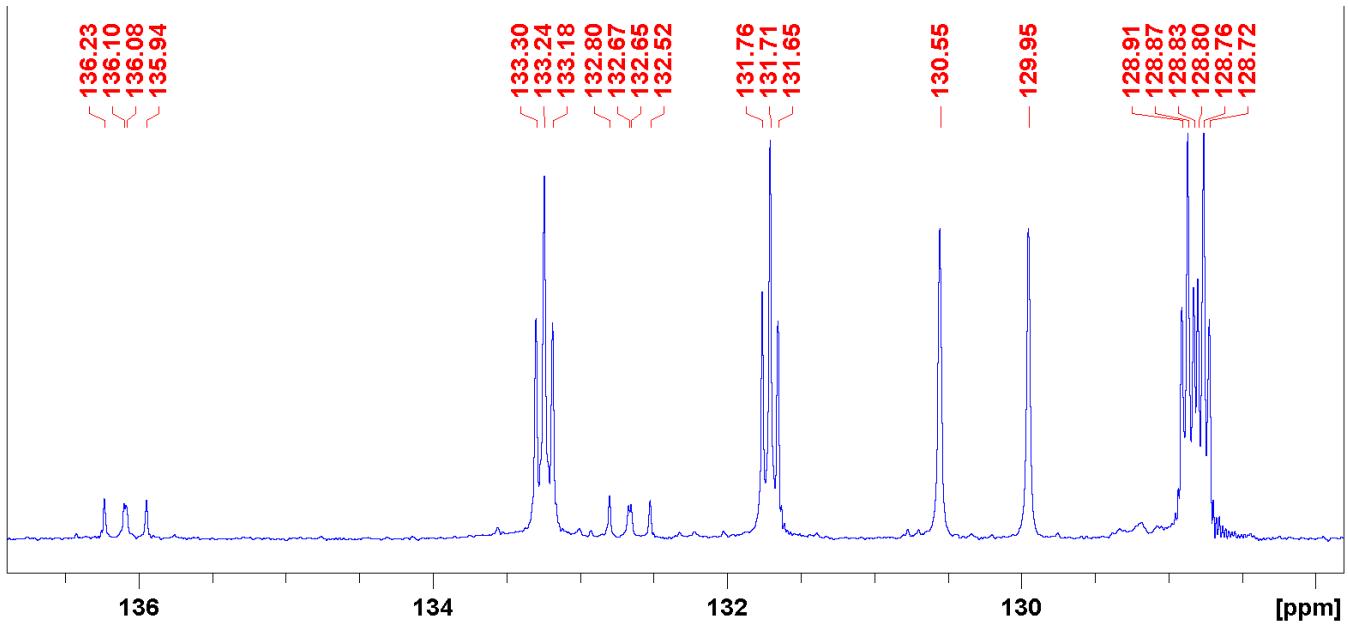


Figure S12. ¹³C NMR spectrum (125 MHz; CDCl₃) of **2**. Expansion of aromatic carbon region.

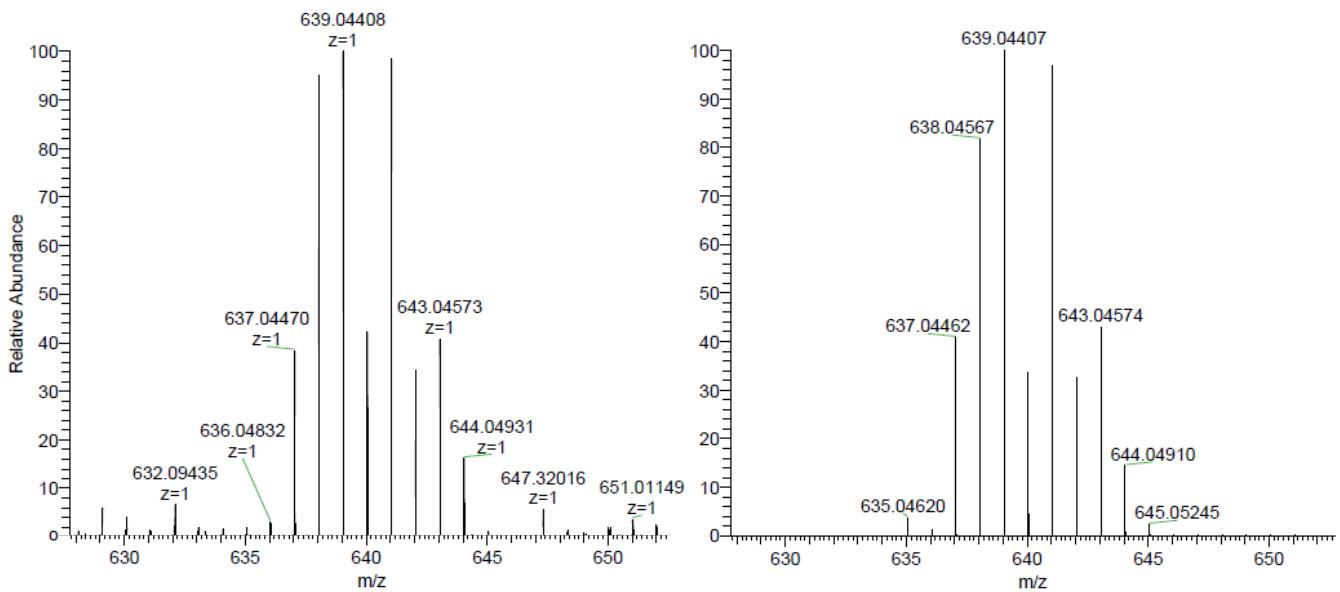
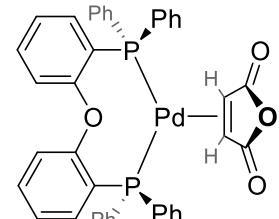


Figure S13. *Left:* Experimental HRMS-ESI spectrum of $[2\bullet\text{Na}]^+$. *Right:* Calculated HRMS isotope pattern for $[2\bullet\text{Na}]^+$.

DPEPhos-Pd-MAH (3)

Prepared according to the general procedure using **1** (100.0 mg, 0.2133 mmol), DPEPhos (120.6 mg, 0.2240 mmol), and THF (5 mL). Trituration/decantation 3 x with diethyl ether (4 mL). Tan solid: 135.7 mg (86%). Crystals for X-ray diffraction were grown at room temperature from DCM/Et₂O (Et₂O as anti-solvent) by layering Et₂O on top of a concentrated solution of **3** in DCM. ¹H NMR: (500 MHz; CD₂Cl₂) δ 4.09 (m, 2H, $-\text{CH}=\text{CH}-$), 6.67 (m, 2H, Ar-H), 6.93 (t, 2H, $J = 7.6$ Hz), 6.99 (dd, 2H, $J = 3.7, 8.4$ Hz), 7.26-7.46 (m, 24H, Ar-H); ¹³C{¹H} NMR: (125 MHz; CD₂Cl₂) δ 54.9 (m), 120.6, 124.6 (t, $J = 2.6$ Hz), 124.9 (m), 128.4 (t, $J = 4.7$ Hz), 129.7, 130.2, 131.3 (m), 131.6, 133.3 (t, $J = 6.8$ Hz), 133.4 (m), 134.2 (t, $J = 7.5$ Hz), 158.5 (t, $J = 4.8$ Hz), 170.1; ³¹P{¹H} NMR: (202 MHz; CD₂Cl₂) δ 16.6. HRMS (ESI) of $[\text{C}_{40}\text{H}_{30}\text{O}_4\text{P}_2\text{Pd}\bullet\text{Na}]^+$ (major isotopomer, sodium adduct): 765.05463 (calc'd); 765.05497 (found). Elemental analysis (CH) of $\text{C}_{40}\text{H}_{30}\text{O}_4\text{P}_2\text{Pd}$: 64.66, 4.07 (calc'd); 64.63, 4.18 (actual).



DPEPhos-Pd-MAH (3)
86% isolated

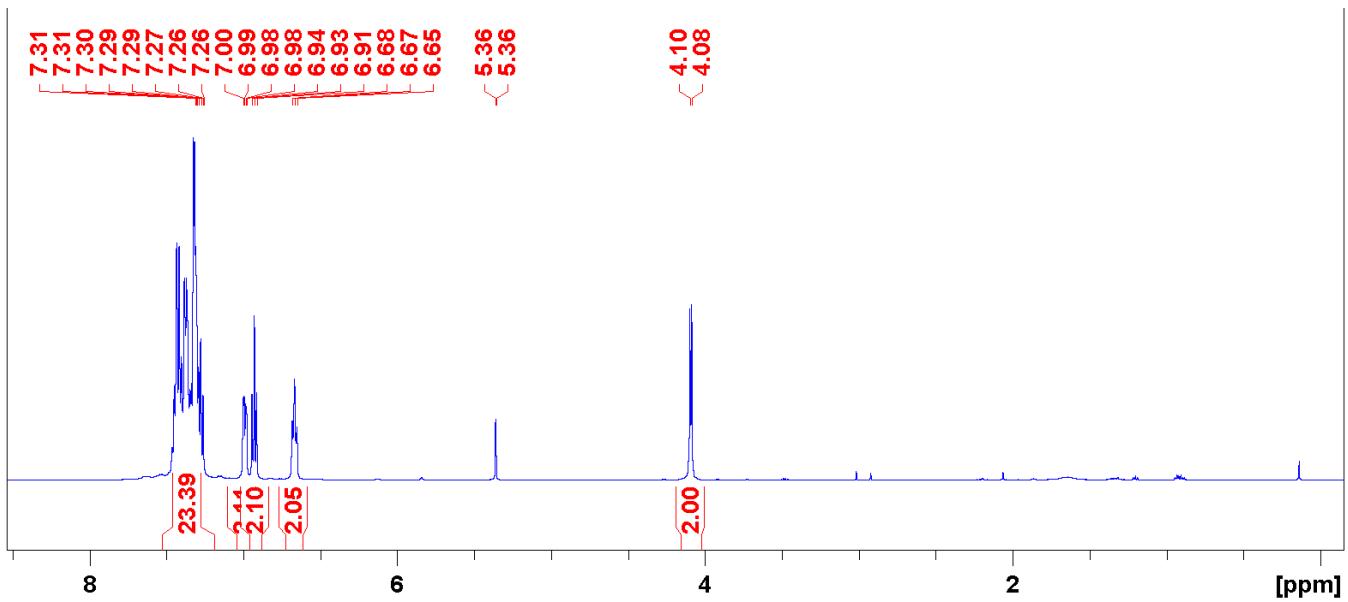


Figure S14. ^1H NMR spectrum (500 MHz; CD_2Cl_2) of 3.

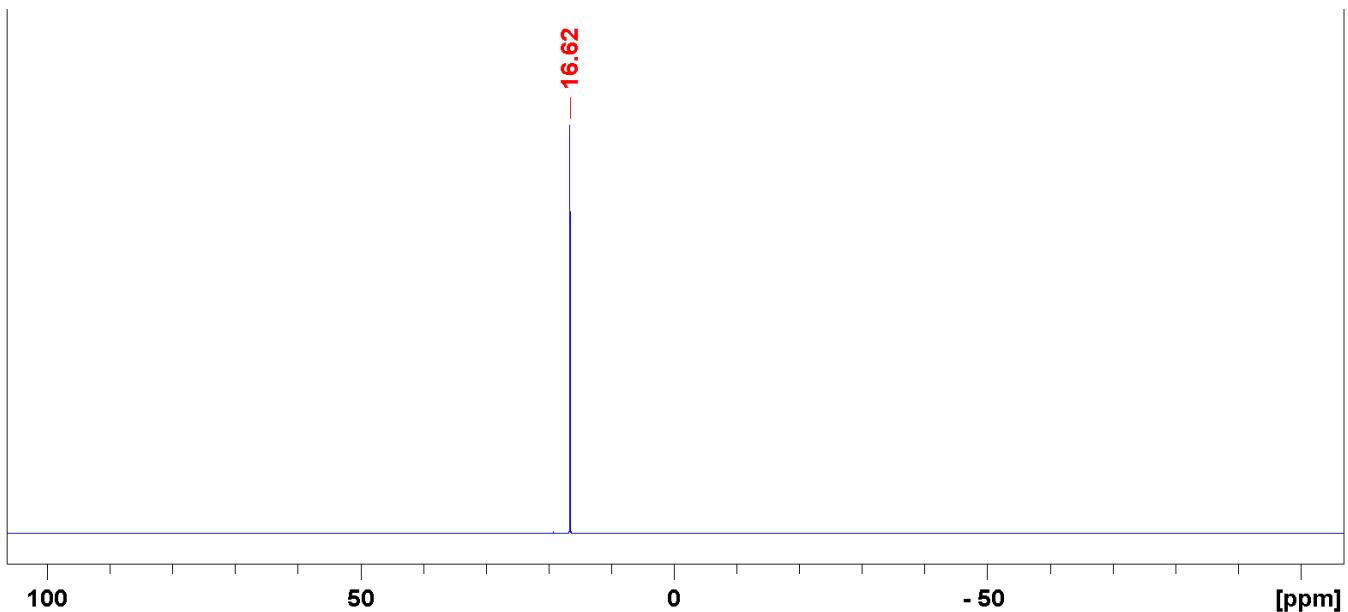


Figure S15. ^{31}P NMR spectrum (202 MHz; CD_2Cl_2) of 3.

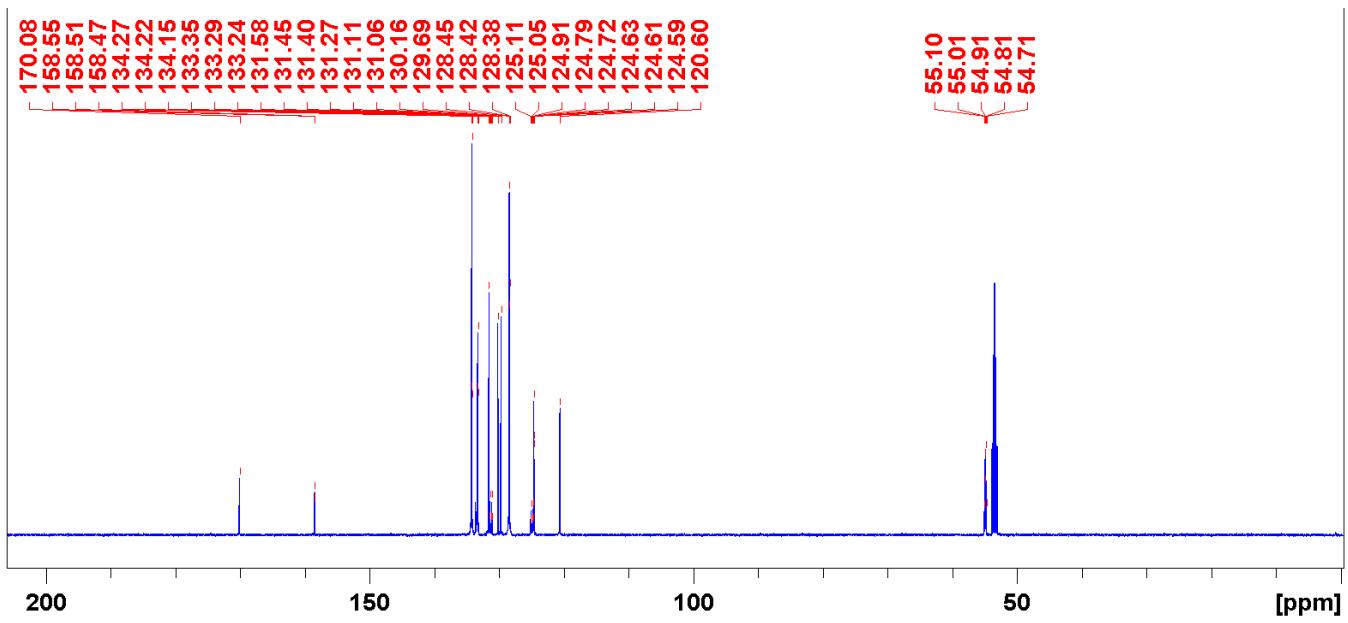


Figure S16. ^{13}C NMR spectrum (125 MHz; CD_2Cl_2) of **3**.

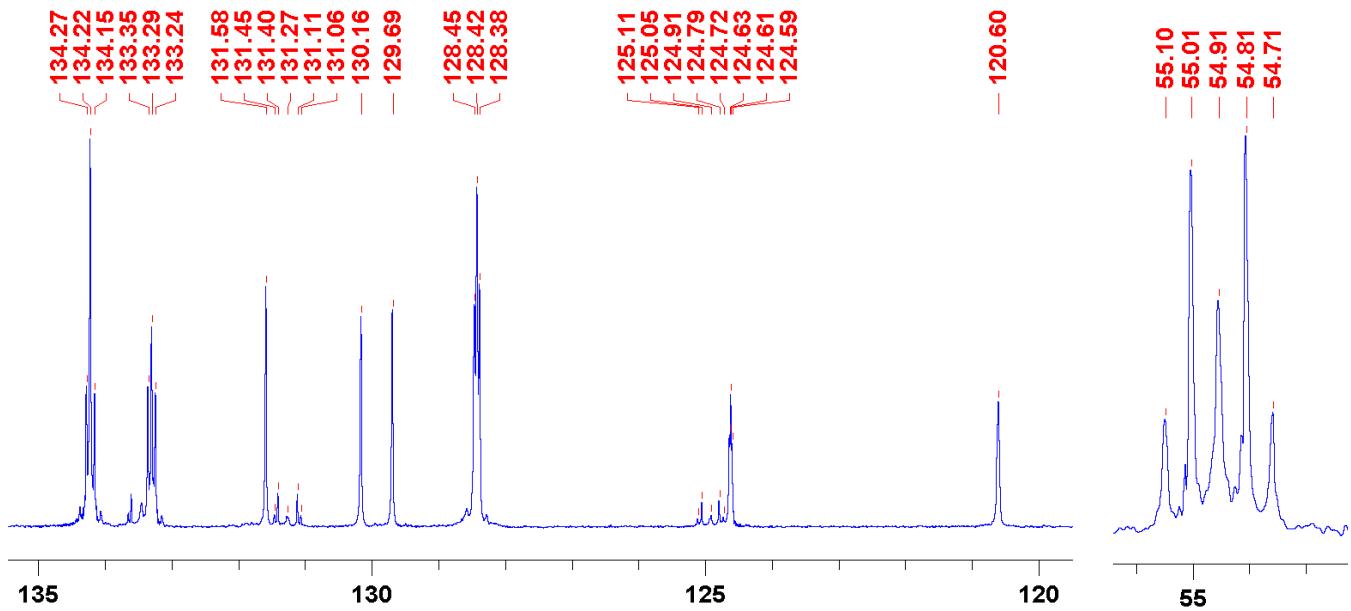


Figure S17. ^{13}C NMR spectrum (125 MHz; CD_2Cl_2) of **3**. Expansions showing multiplets.

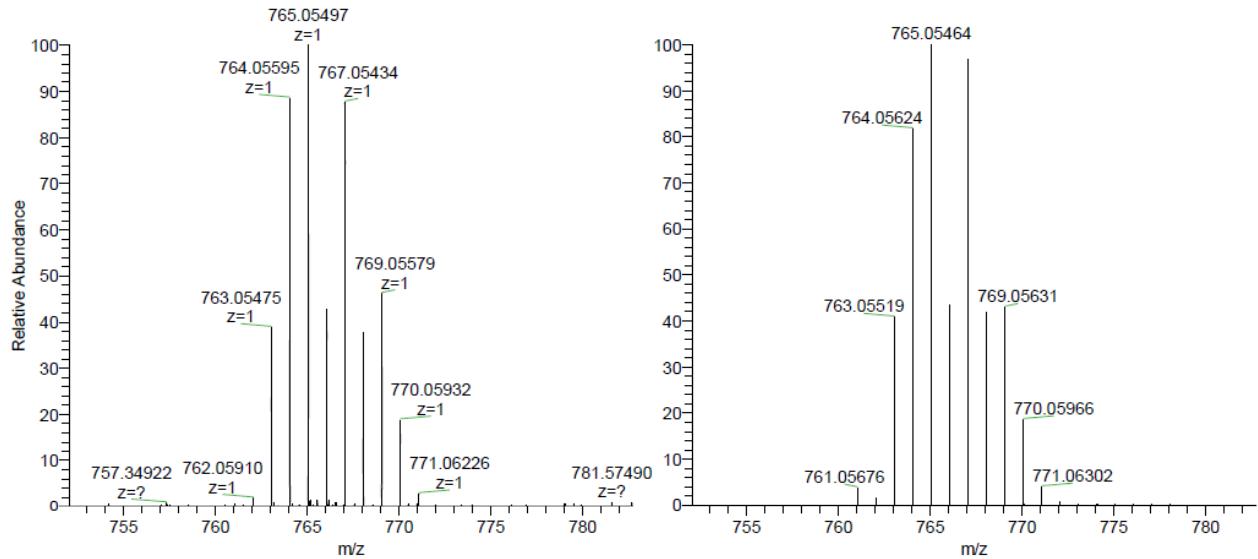


Figure S18. *Left:* Experimental HRMS-ESI spectrum of $[3 \bullet \text{Na}]^+$. *Right:* Calculated HRMS isotope pattern for $[3 \bullet \text{Na}]^+$.

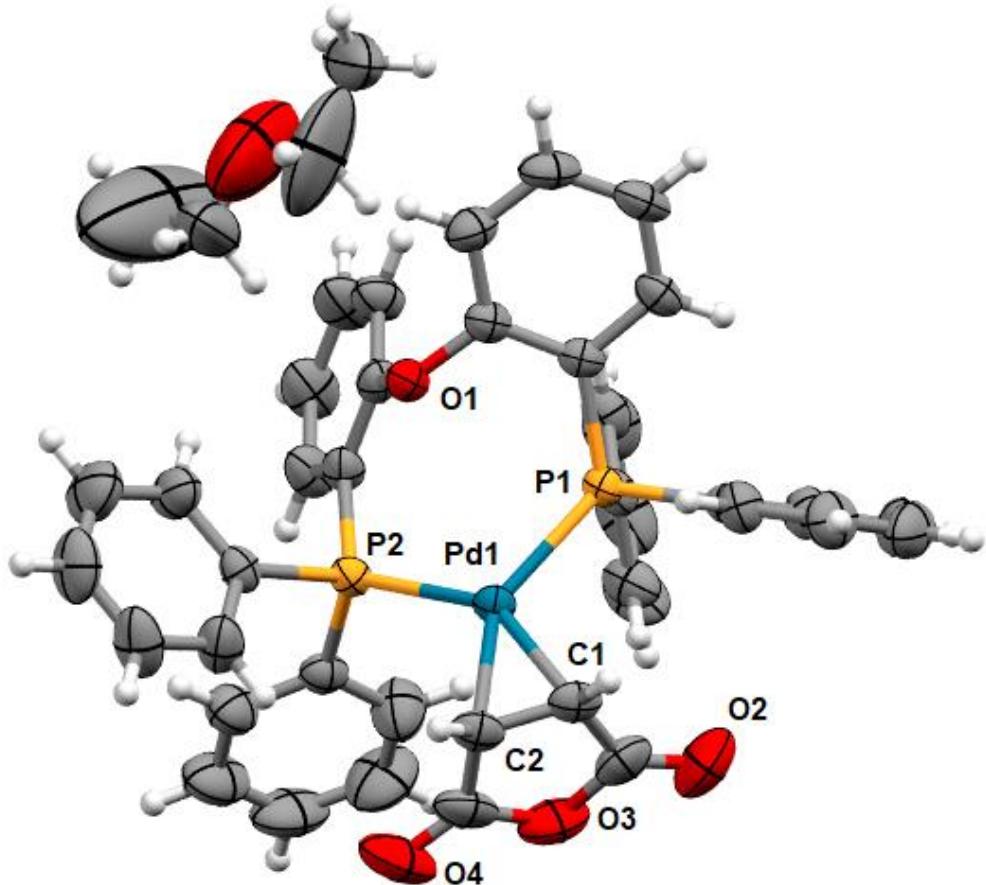
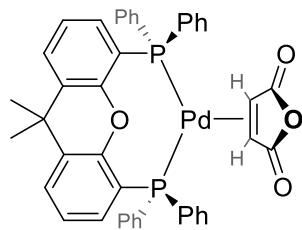


Figure S19. Solid-state molecular structure of complex **3**, including diethyl ether solvate. Thermal ellipsoids plotted at 50% probability for non-H atoms; H-atoms shown as uniformly-sized white spheres for clarity. X-ray diffraction data collected at room temperature. Selected bond lengths (\AA) and angles ($^\circ$): Pd1-P1 : 2.3140(10); Pd1-P2 : 2.3211(10); Pd1-C1 : 2.104(4); Pd1-C2 : 2.125(4); C1-C2 : 1.396(6); P1-Pd1-P2 : 106.32(3); C1-Pd1-C2 : 38.55(15); C1-Pd1-P1 : 106.38(12); C2-Pd1-P2 : 108.67(12).

XantPhos–Pd–MAH (**4**)

Prepared according to the general procedure using **1** (100.0 mg, 0.2133 mmol), XantPhos (129.6 mg, 0.2240 mmol), and THF (5 mL). Trituration/decantation 3 x with THF (4 mL). White solid: 147.7 mg (81%). Compound isolated as the THF solvate (**1** equiv THF, as observed by ^1H NMR spectroscopy, remains after extensive vacuum drying of the isolated solid). Crystals for X-ray diffraction were grown at room temperature from DCM/Et₂O (Et₂O as anti-solvent) by layering Et₂O on top of a concentrated solution of **4** in DCM. ^1H NMR: (500 MHz; CDCl₃) δ 1.47 (s, 3H, $-\text{CH}_3$), 1.87 (m, 4H, THF), 1.89 (s, 3H, $-\text{CH}_3$), 3.77 (m, 4H, THF), 3.98 (m, 2H, $-\text{CH}=\text{CH}-$), 6.54 (td, 2H, $J = 1.0, 8.0$ Hz), 7.09–7.28 (m, 16H, Ar–H), 7.42 (t, 4H, $J = 7.4$ Hz), 7.46 (t, 2H, $J = 7.4$ Hz), 7.55 (dd, 2H, $J = 1.0, 8.0$ Hz); $^{13}\text{C}\{\text{H}\}$ NMR: (125 MHz; CDCl₃) δ 23.9, 25.6 (THF), 31.6, 36.0, 56.8 (m), 68.0 (THF), 121.2 (m), 124.4 (t, $J = 2.6$ Hz), 126.7, 128.2 (m), 128.4 (m), 129.5, 129.8, 130.8 (m), 131.7, 132.9 (m), 133.5 (m), 133.9 (m), 155.4 (t, $J = 5.2$ Hz), 169.8; $^{31}\text{P}\{\text{H}\}$ NMR: (202 MHz; CDCl₃) δ 10.7. HRMS (ESI) of [C₄₃H₃₄O₄P₂Pd•H]⁺ (major isotopomer, proton adduct): 783.10399 (calc'd); 783.10406 (found). Elemental analysis (CH) of C₄₇H₄₂O₅P₂Pd (**4**•THF): 66.01, 4.95 (calc'd); 66.67, 4.94 (actual).



XantPhos-Pd-MAH (4)
81% isolated (THF solvate)

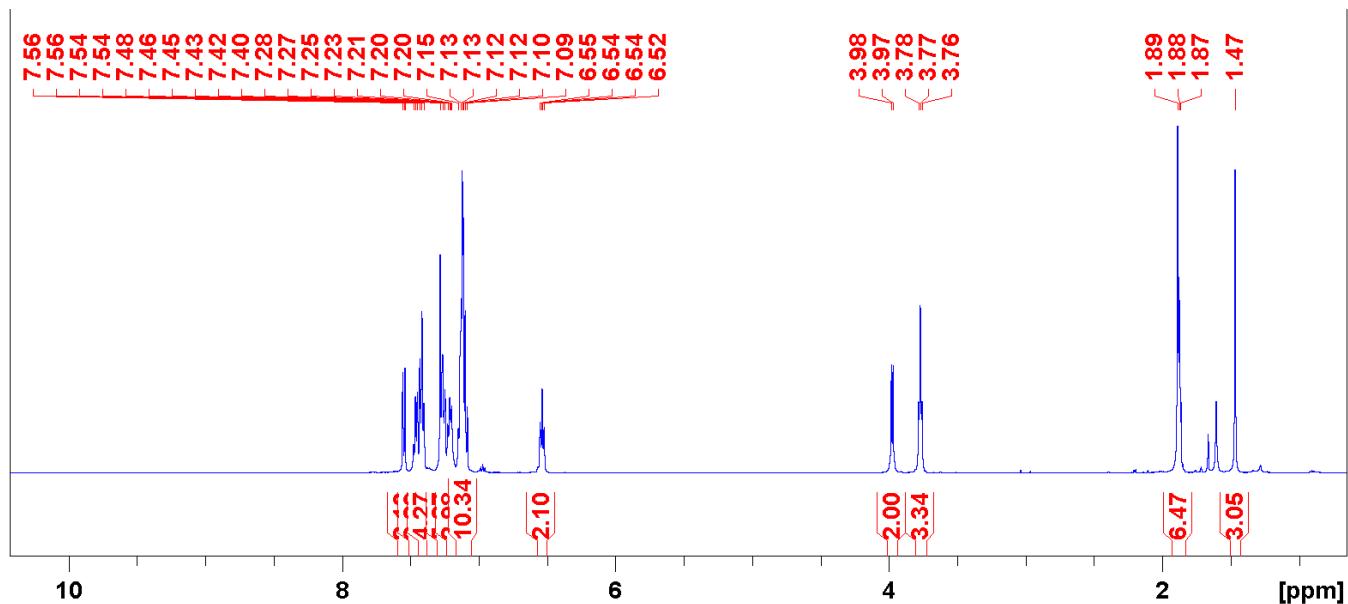


Figure S20. ^1H NMR spectrum (500 MHz; CDCl₃) of **4**.

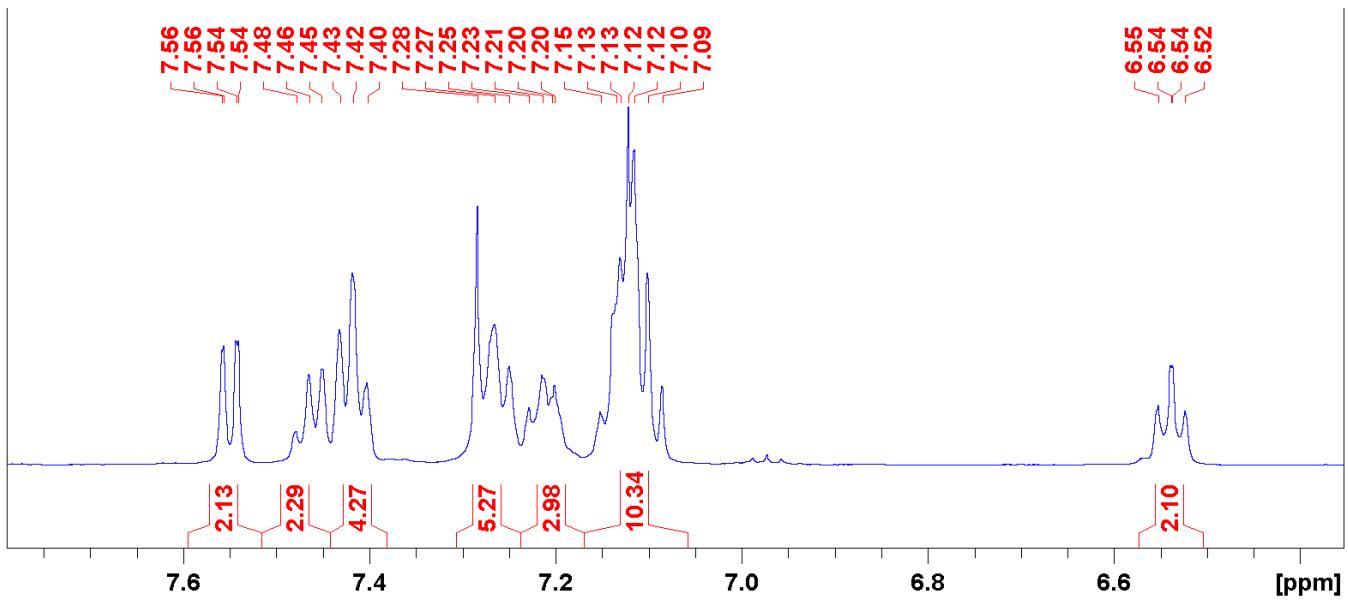


Figure S21. ^1H NMR spectrum (500 MHz; CDCl_3) of **4**. Expansion of aromatic region.

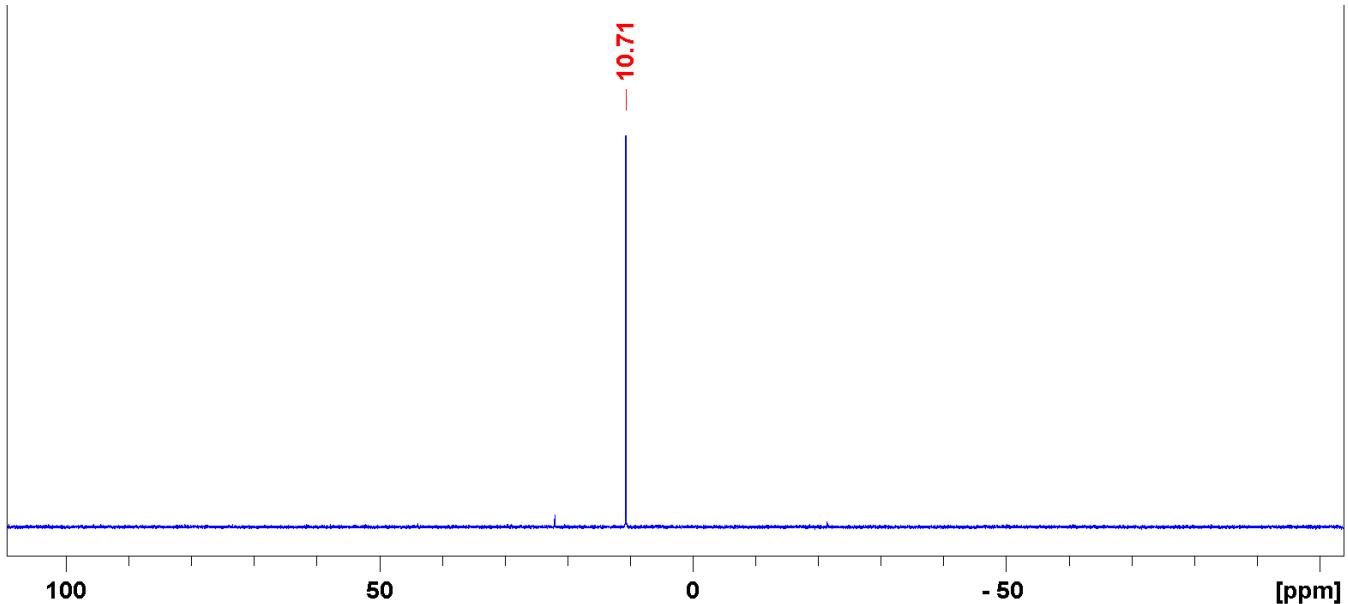


Figure S22. ^{31}P NMR spectrum (202 MHz; CDCl_3) of **4**.

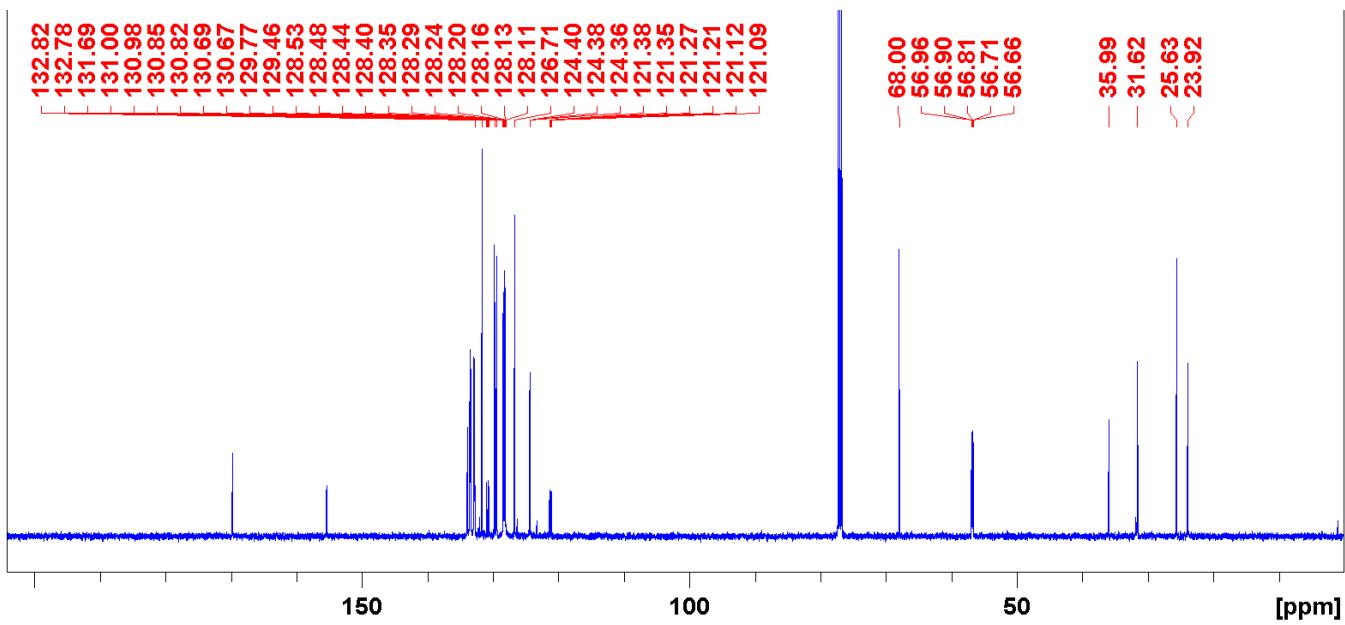


Figure S23. ^{13}C NMR spectrum (125 MHz; CDCl_3) of **4**.

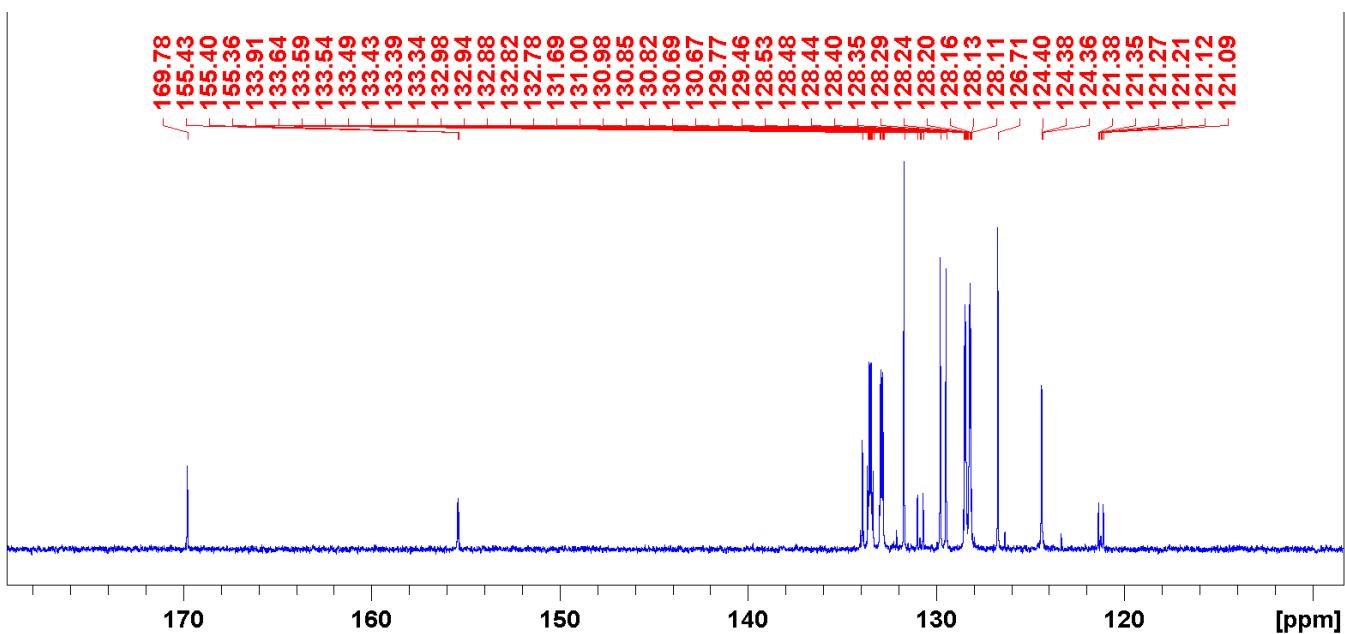


Figure S24. ^{13}C NMR spectrum (125 MHz; CDCl_3) of **4**. Expansion of downfield region.

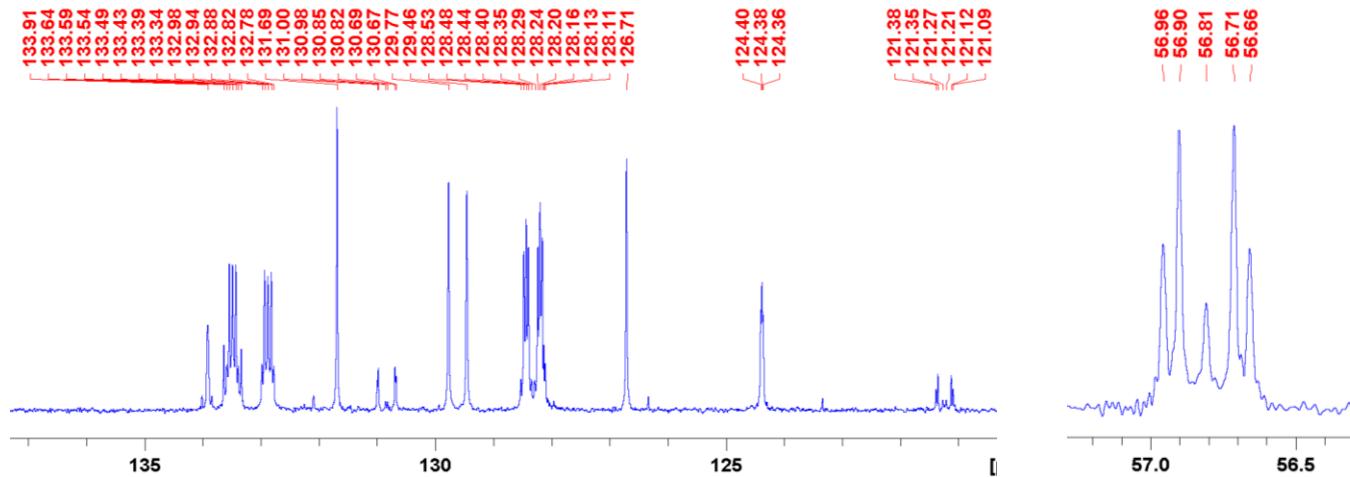


Figure S25. ^{13}C NMR spectrum (125 MHz; CDCl_3) of **4**. Expansions showing multiplets.

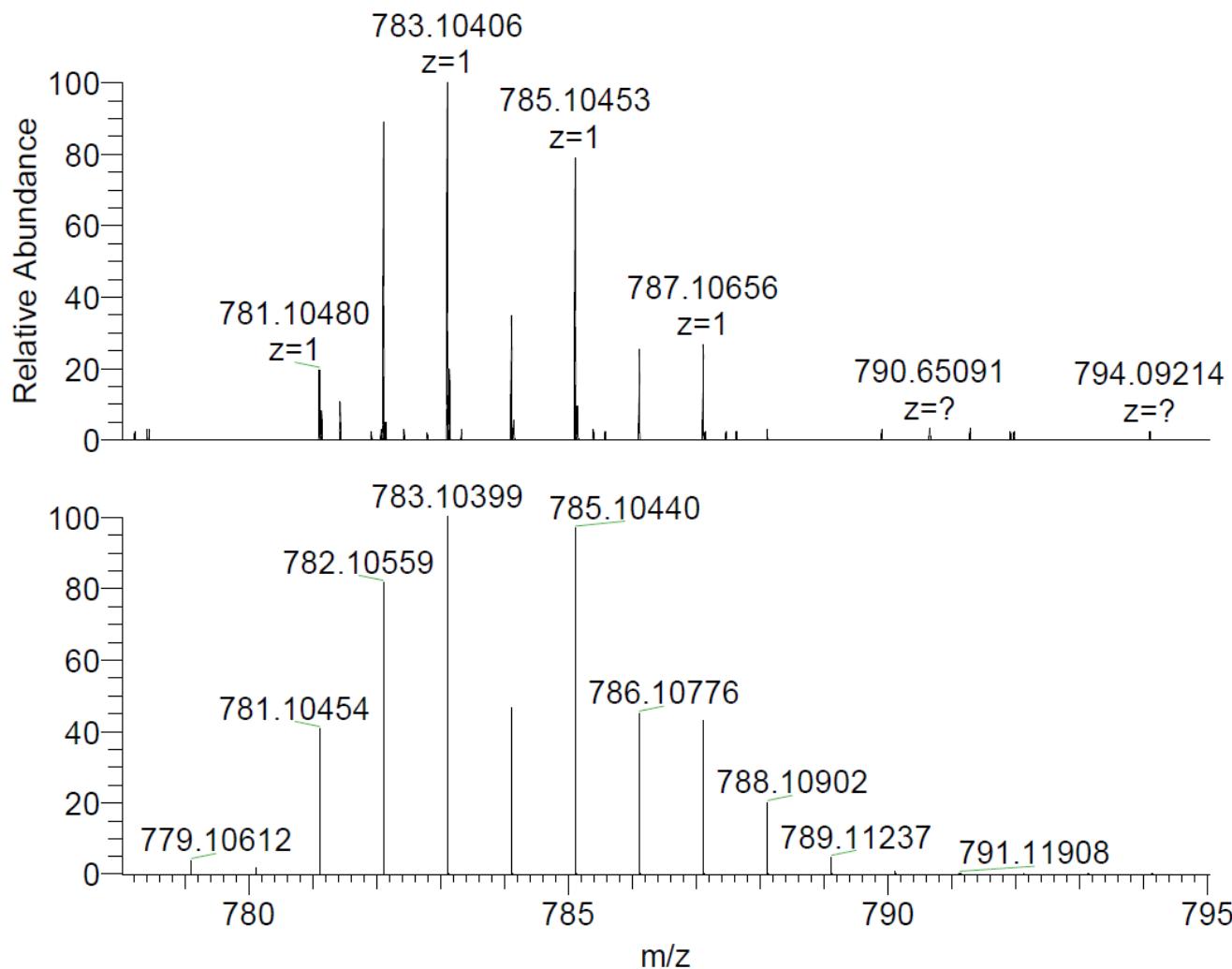


Figure S26. *Top:* Experimental HRMS-ESI spectrum of $[4\bullet\text{H}]^+$. *Bottom:* Calculated HRMS isotope pattern for $[4\bullet\text{H}]^+$.

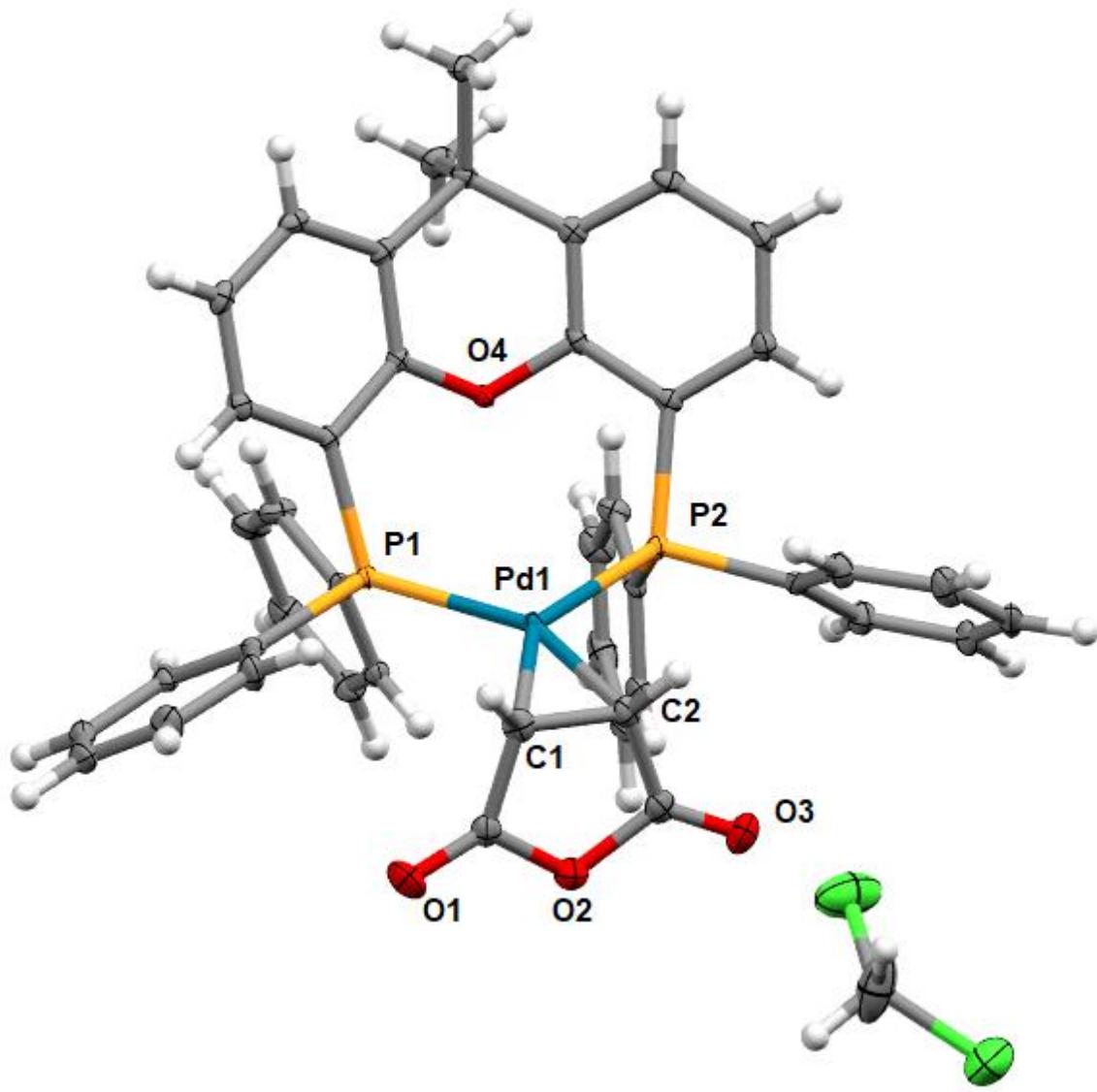
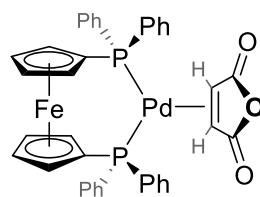


Figure S27. Solid-state molecular structure of complex **4**, including half-occupancy dichloromethane solvate. Thermal ellipsoids plotted at 50% probability for non-H atoms; H-atoms shown as uniformly-sized white spheres for clarity. Selected bond lengths (\AA) and angles ($^{\circ}$): Pd1–P1: 2.3492(7); Pd1–P2: 2.3427(7); Pd1–C1: 2.141(3); Pd1–C2: 2.111(3); C1–C2: 1.420(4); P1–Pd1–P2: 106.32(3); C1–Pd1–C2: 39.01(11); C1–Pd1–P1: 110.43(8); C2–Pd1–P2: 104.24(8).

dppf–Pd–MAH (5)

Prepared according to the general procedure using **1** (100.0 mg, 0.2133 mmol), dppf (124.2 mg, 0.2240 mmol), and THF (5 mL). Trituration/decantation 3 x with diethyl ether (4 mL). Brown solid: 150.0 mg (93%). Crystals for X-ray diffraction were grown at room temperature from DCM/Et₂O (Et₂O as anti-solvent) by layering Et₂O on top of a concentrated solution of **5** in DCM. ¹H NMR: (300 MHz; CDCl₃) δ 4.11 (br m, 2H, –CH=CH–), 4.19 (br m, 4H, Cp–H), 4.33 (br m, 4H, Cp–H), 7.42 (br m, 12H, Ph–H), 7.52 (br m, 4H, Ph–H), 7.65 (br m, 4H, Ph–H); ¹³C{¹H} NMR: (125 MHz; CDCl₃) δ 53.8 (m), 72.4, 74.6, 128.5 (d, *J* = 13.4 Hz), 130.2 (d, *J* = 48.0 Hz), 133.8 (m), 136.6 (m), 170.7; ³¹P{¹H} NMR: (202 MHz; CDCl₃) δ 22.9. HRMS (ESI) of [C₃₈H₃₀FeO₃P₂Pd•Na]⁺ (major isotopomer, Na⁺ adduct): 780.99466 (calc'd); 780.99434 (found). Elemental analysis (CH) of C₃₈H₃₀FeO₃P₂Pd: 60.14, 3.98 (calc'd); 60.08, 4.08 (actual).



dppf-Pd-MAH (5)
93% isolated

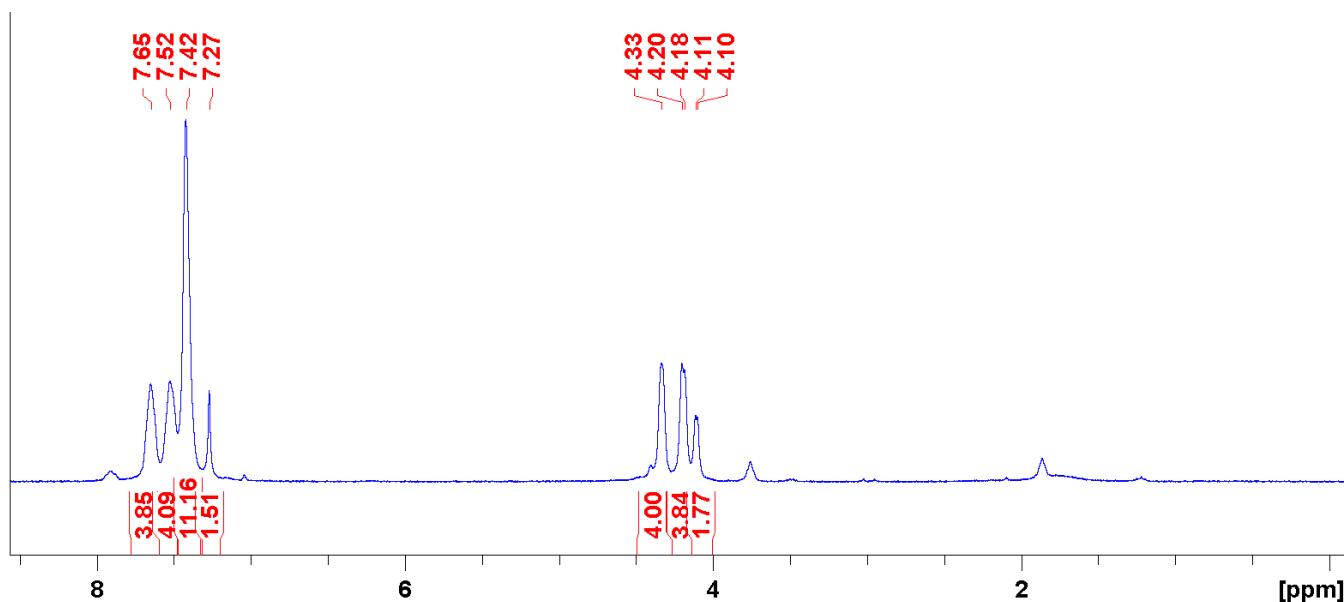


Figure S28. ¹H NMR spectrum (300 MHz; CDCl₃) of **5**.

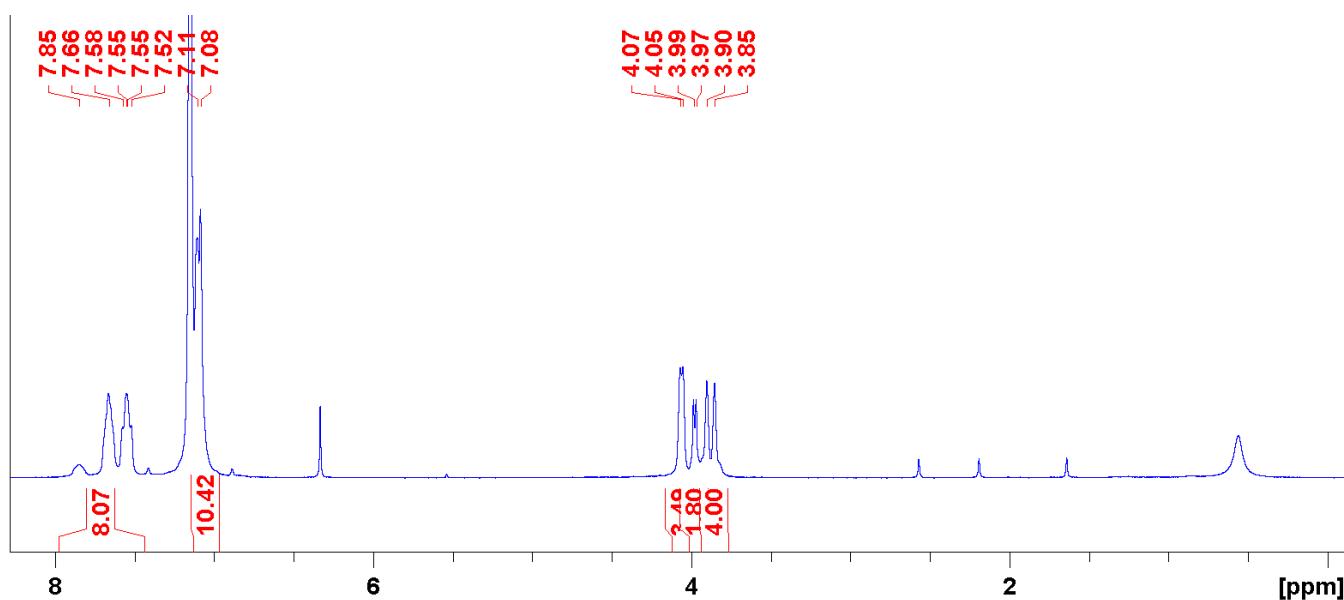


Figure S29. ¹H NMR spectrum (300 MHz; C₆D₆) of **5**, giving better peak resolution.

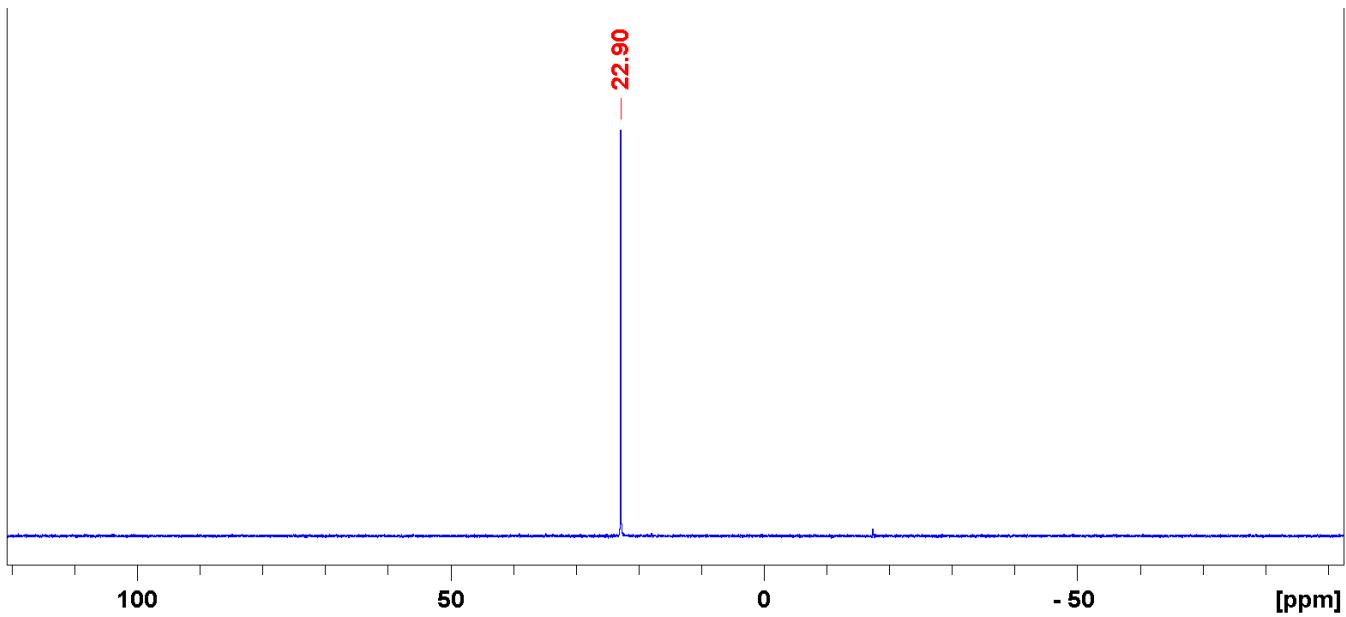


Figure S30. ^{31}P NMR spectrum (121 MHz; CDCl_3) of 5.

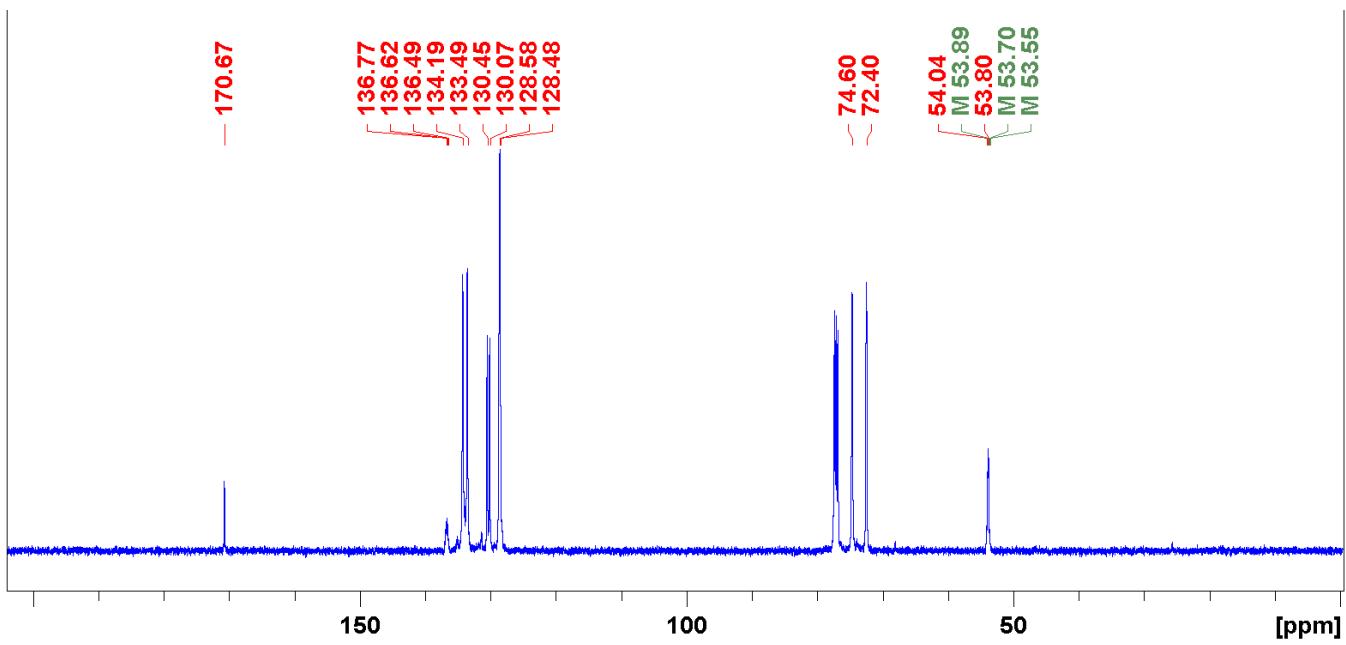


Figure S31. ^{13}C NMR spectrum (125 MHz; CDCl_3) of 5 (green labels are manually-picked peaks in the multiplet).

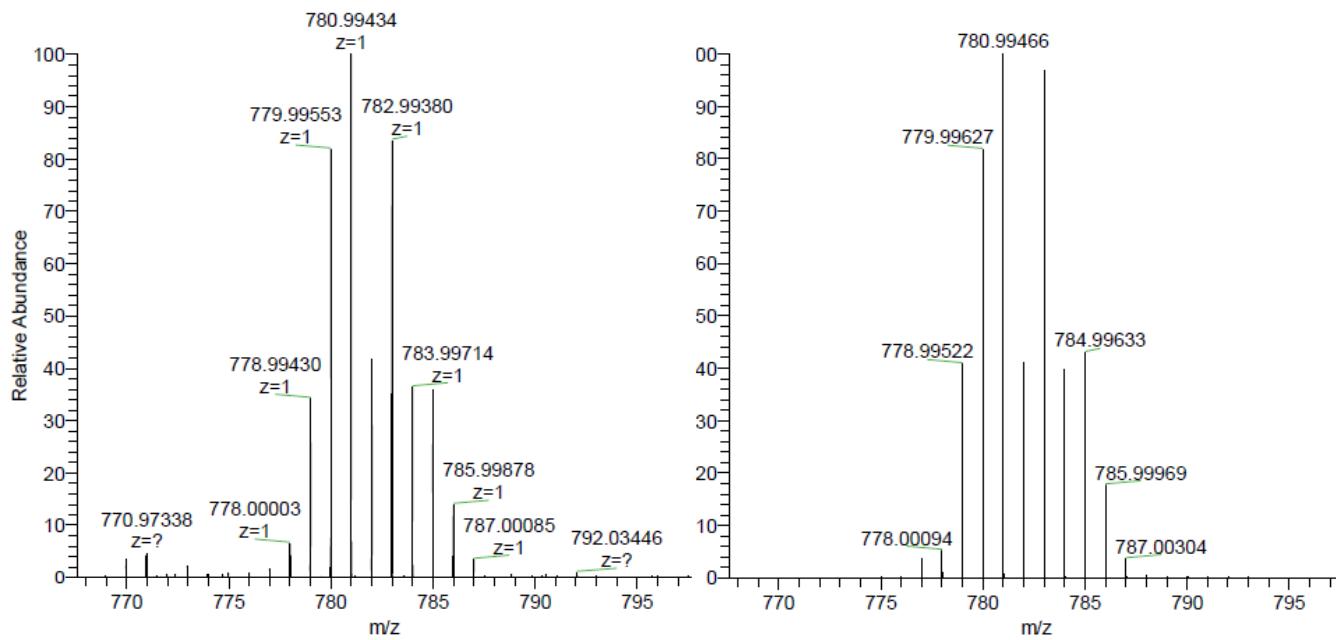


Figure S32. *Left:* Experimental HRMS-ESI spectrum of $[5 \bullet \text{Na}]^+$. *Right:* Calculated HRMS isotope pattern for $[5 \bullet \text{Na}]^+$.

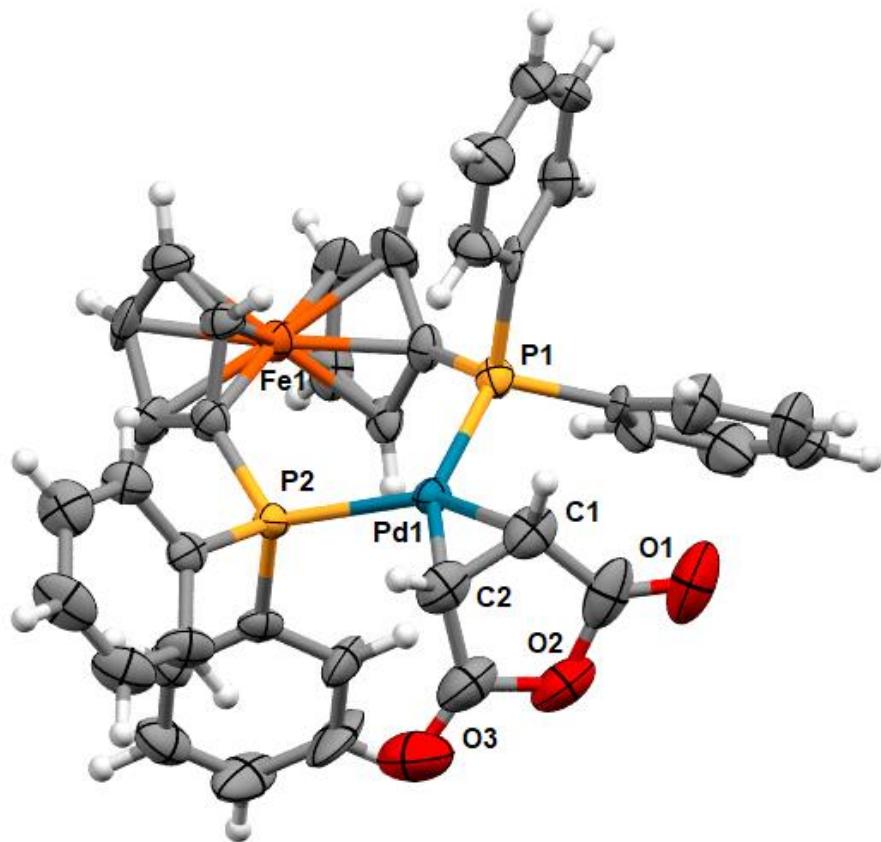
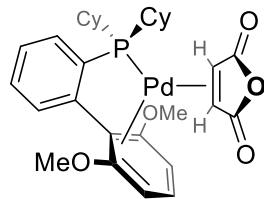


Figure S33. Solid-state molecular structure of complex 5. Thermal ellipsoids plotted at 50% probability for non-H atoms; H-atoms shown as uniformly-sized white spheres for clarity. X-ray diffraction data collected at room temperature. Selected bond lengths (\AA) and angles ($^\circ$): Pd1–P1: 2.324(4); Pd1–P2: 2.302(4); Pd1–C1: 2.140(16); Pd1–C2: 2.105(16); C1–C2: 1.39(2); P1–Pd1–P2: 105.16(13); C1–Pd1–C2: 38.3(6); C1–Pd1–P1: 113.5(5); C2–Pd1–P2: 102.9(5).

SPhos-Pd-MAH (**6**)

Prepared according to the general procedure using **1** (100.0 mg, 0.2133 mmol), SPhos (91.9 mg, 0.2240 mmol), and THF (5 mL). Trituration/decantation 3 x with diethyl ether (4 mL). Yellow solid: 86.6 mg (66%). ^1H NMR: (300 MHz; CDCl_3) δ 1.10-1.40 (m, 10H, Cy-H), 1.60-1.96 (br m, 10H, Cy-H), 2.12 (br m, 2H, Cy-H), 3.69 (s, 6H, 2 x OCH_3), 4.5 (v br, 1H, $-\text{CH}=\text{CH}-$), 6.91 (m, 3H, Ar-H), 7.37-7.46 (m, 3H, Ar-H), 7.60 (m, 1H, Ar-H); $^{13}\text{C}\{\text{H}\}$ NMR: (75 MHz; CDCl_3) δ 26.1, 27.0 (d, J = 11.1 Hz), 28.9 (m), 29.5 (br), 34.3 (d, J = 19.0), 54.7 (br), 55.8, 105.3 (br), 127.5 (d, J = 4.0 Hz), 129.4, 130.7 (d, J = 2.1 Hz), 130.9 (d, J = 11.1 Hz), 132.0, 137.3 (d, 31.0 Hz), 143.8, 144.2, 153.6; $^{31}\text{P}\{\text{H}\}$ NMR: (121 MHz; CDCl_3) δ 44.2. HRMS (ESI) of $[\text{C}_{30}\text{H}_{37}\text{O}_5\text{PPd}\bullet\text{H}]^+$ (major isotopomer, H^+ adduct): 615.14862 (calc'd); 615.14870 (found). Elemental analysis (CH) of $\text{C}_{30}\text{H}_{37}\text{O}_5\text{PPd}$: 58.59, 6.06 (calc'd); 58.47, 6.07 (actual).



SPhos-Pd-MAH (6)
66% isolated

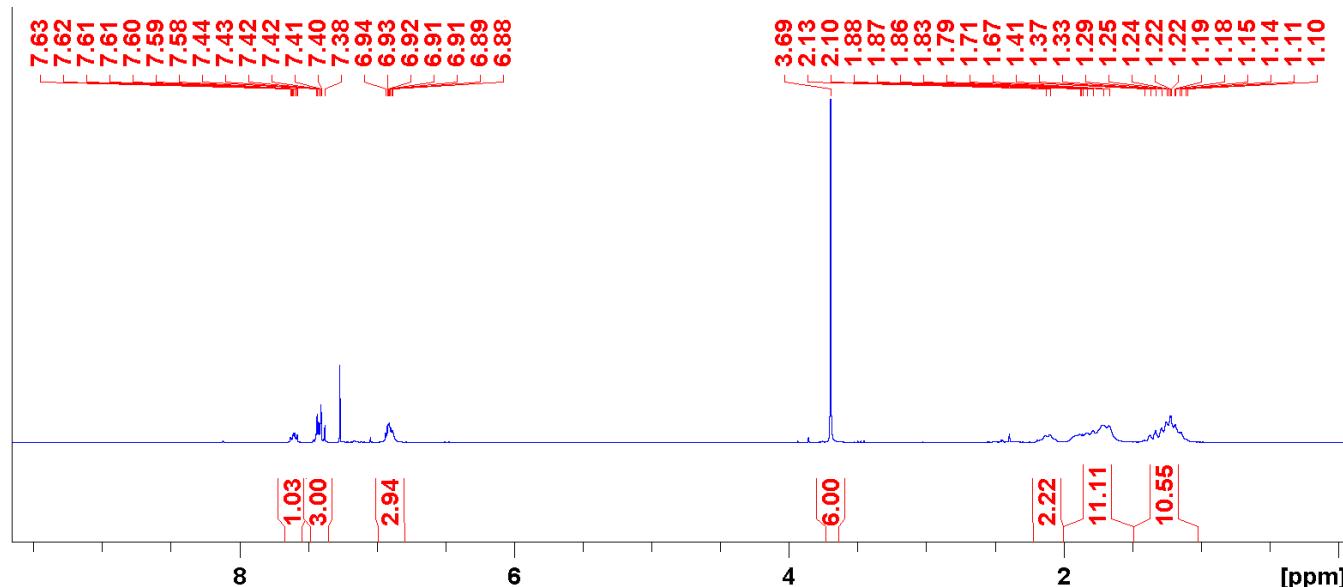


Figure S34. ^1H NMR spectrum (300 MHz; CDCl_3) of **5**.

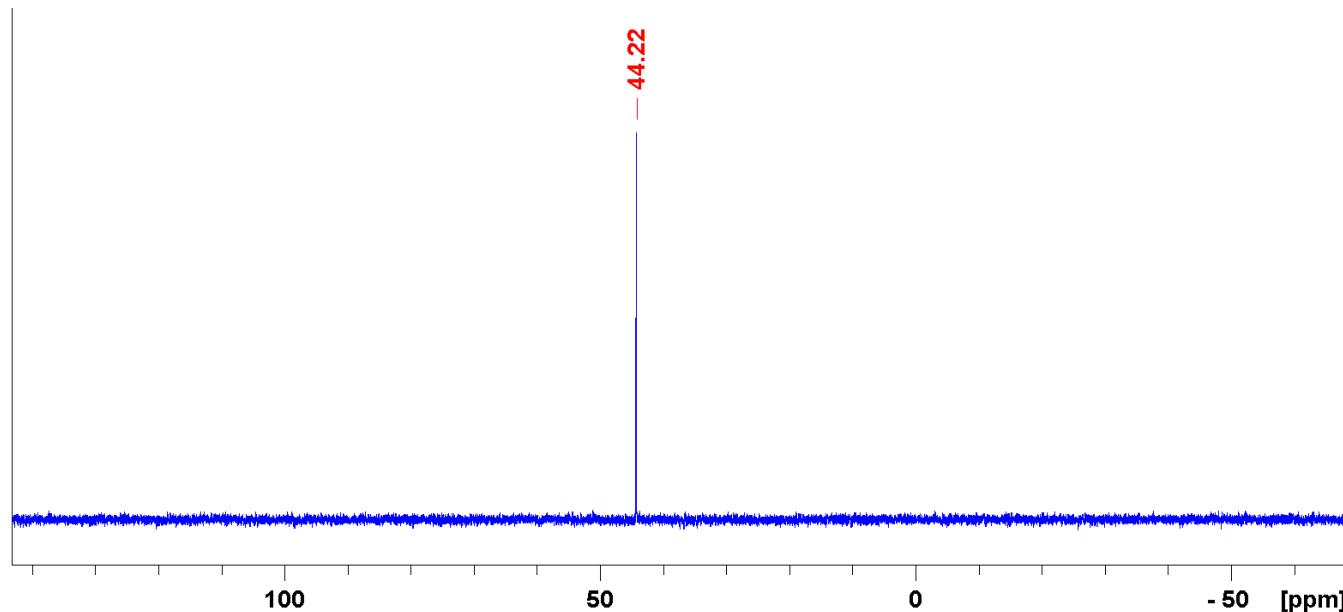


Figure S35. ^{31}P NMR spectrum (121 MHz; CDCl_3) of **6**.

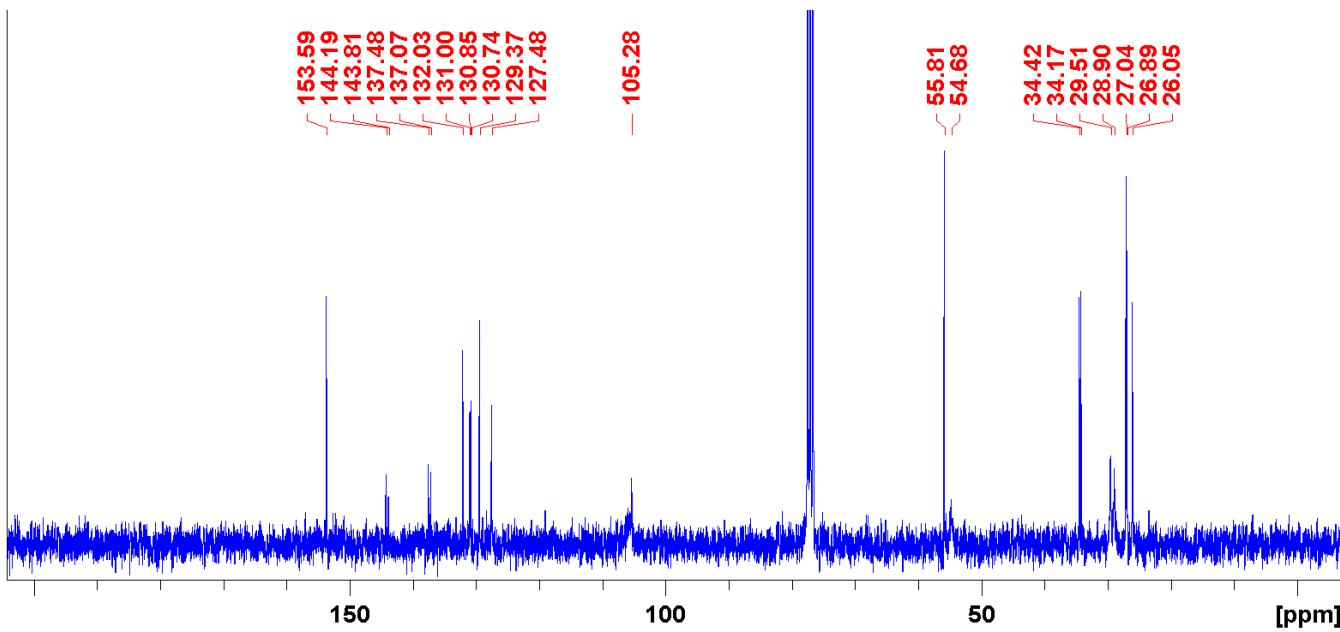


Figure S36. ^{13}C NMR spectrum (75 MHz; CDCl_3) of **6**.

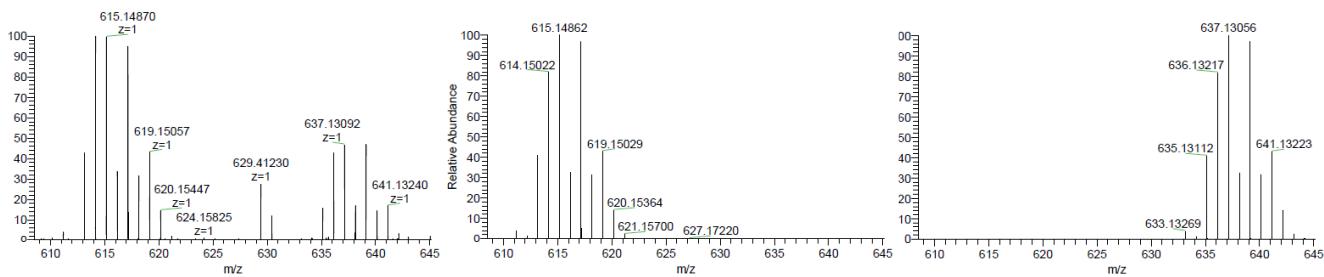
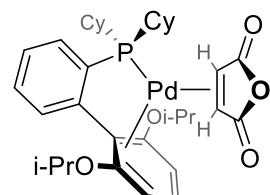


Figure S37. *Left:* Experimental HRMS-ESI spectrum of $[6\bullet\text{H}]^+$ and $[6\bullet\text{Na}]^+$. *Middle:* Calculated HRMS isotope pattern for $[6\bullet\text{H}]^+$. *Right:* Calculated HRMS isotope pattern for $[6\bullet\text{Na}]^+$.

RuPhos-Pd-MAH (7)

Prepared according to the general procedure using **1** (99.3 mg, 0.2118 mmol), RuPhos (98.8 mg, 0.2118 mmol), and THF (15 mL). Trituration/decantation 6 x with hexanes (4 mL). Yellow solid: 86.8 mg (61%). ^1H NMR: (500 MHz, CD_2Cl_2) δ 1.01 (d, 6H, $J = 5.9$ Hz, O-CH(CH_3)₂), 1.11-1.43 (m, 10H, Cy-H), 1.26 (d, 6H, $J = 5.9$ Hz, O-CH(CH_3)₂), 1.60-1.80 (m, 6H, Cy-H), 1.60-1.80 (m, 6H), 1.85 (m, 2H, Cy-H), 2.00 (m, 2H, Cy-H), 2.13 (m, 2H, Cy-H), 2.50 (br s, 1H, -CH=CH-), 4.50 (br s, 1H, -CH=CH-), 4.55 (sept, 2H, $J = 5.8$ Hz, 2 x O-CH(CH_3)₂), 6.80 (d, 2H, $J = 8.3$ Hz, Ar-H), 6.83-6.89 (m, 1H, Ar-H), 7.35 (t, 1H, $J = 8.3$ Hz, Ar-H), 7.38-7.44 (m, 2H, Ar-H), 7.57-7.63 (m, 1H, Ar-H); $^{13}\text{C}\{\text{H}\}$ NMR: (500 MHz, CD_2Cl_2) δ 21.2, 21.7, 25.6, 26.2, 26.8 (d, $J = 11.1$ Hz), 26.8 (d, $J = 13.9$ Hz), 29.4, 29.9, 34.6 (d, $J = 19.3$ Hz), 54.4, 54.5, 70.4, 105.8, 126.8 (d, $J = 3.8$ Hz), 129.4, 130.2, 131.0 (d, $J = 10.8$ Hz), 131.6, 137.9 (d, $J = 32.0$ Hz), 145.5 (d, $J = 28.9$ Hz), 153.1; $^{31}\text{P}\{\text{H}\}$ NMR: (300 MHz, CD_2Cl_2) δ 44.9. HRMS (ESI) of $[\text{C}_{34}\text{H}_{45}\text{O}_5\text{PPd}\bullet\text{Na}]^+$ (major isotopomer, Na⁺ adduct): 693.19317 (calc'd); 693.19345 (found). Elemental analysis (CH) of $\text{C}_{34}\text{H}_{45}\text{O}_5\text{PPd}$: 60.85, 6.76 (calc'd); 60.75, 6.66 (actual).



RuPhos-Pd-MAH (7)
61% isolated

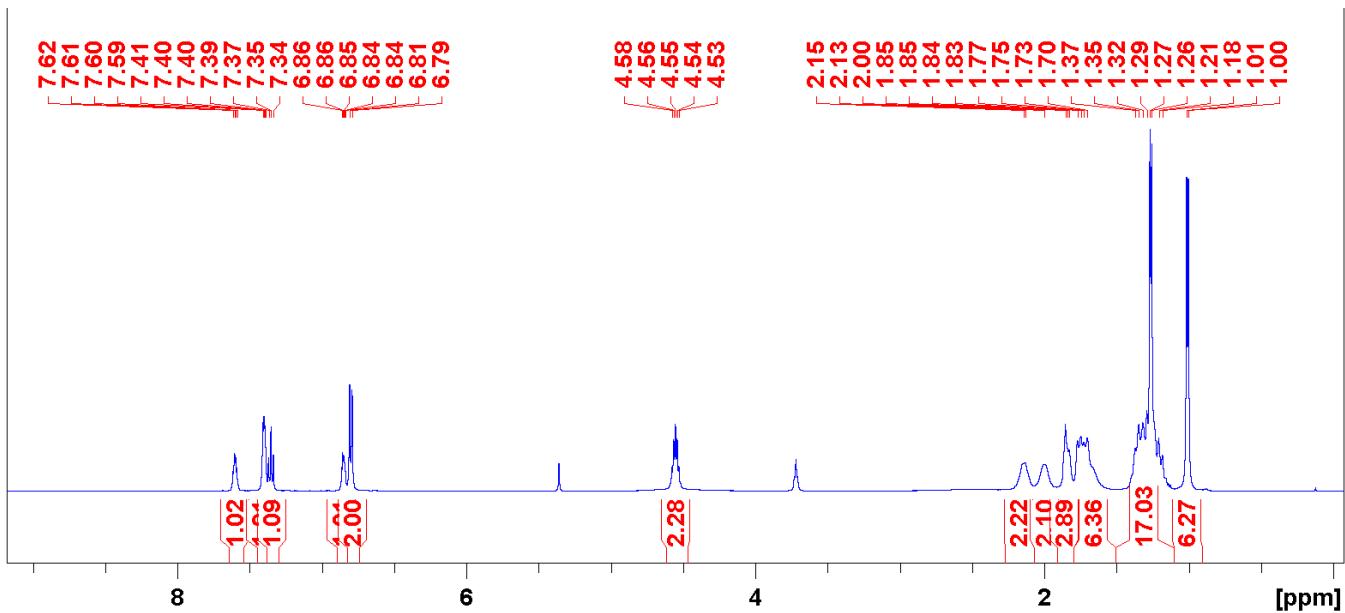


Figure S38. ^1H NMR spectrum (500 MHz; CD_2Cl_2) of 7.

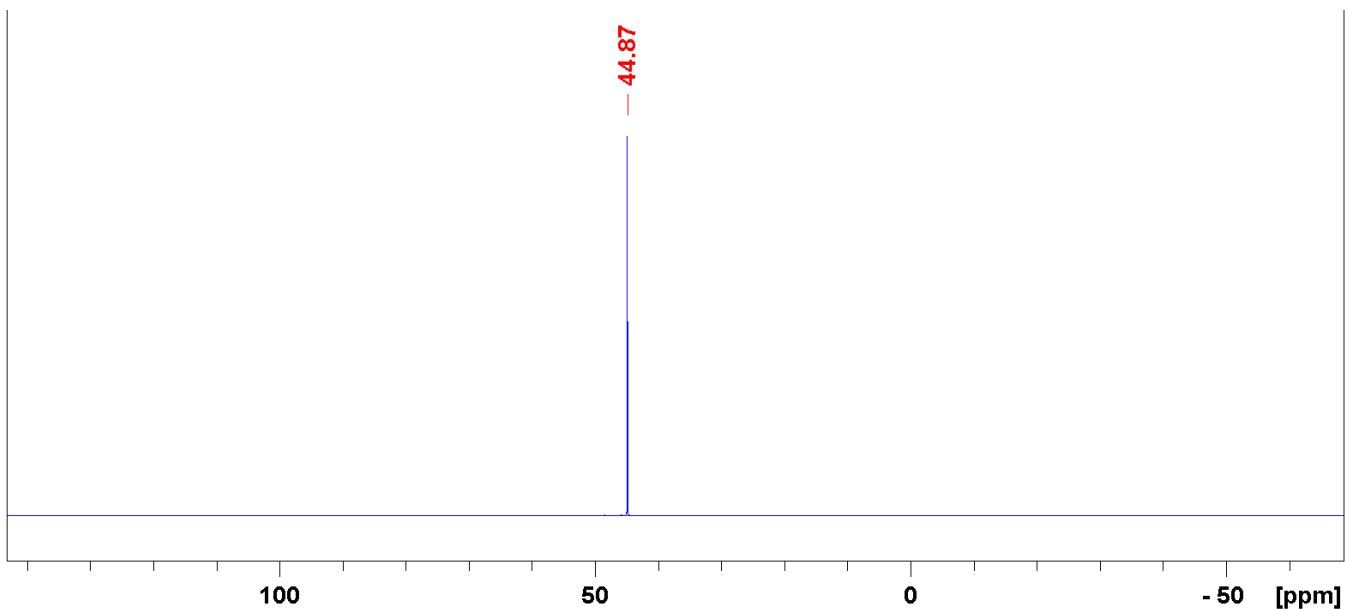


Figure S39. ^{31}P NMR spectrum (202 MHz; CD_2Cl_2) of 7.

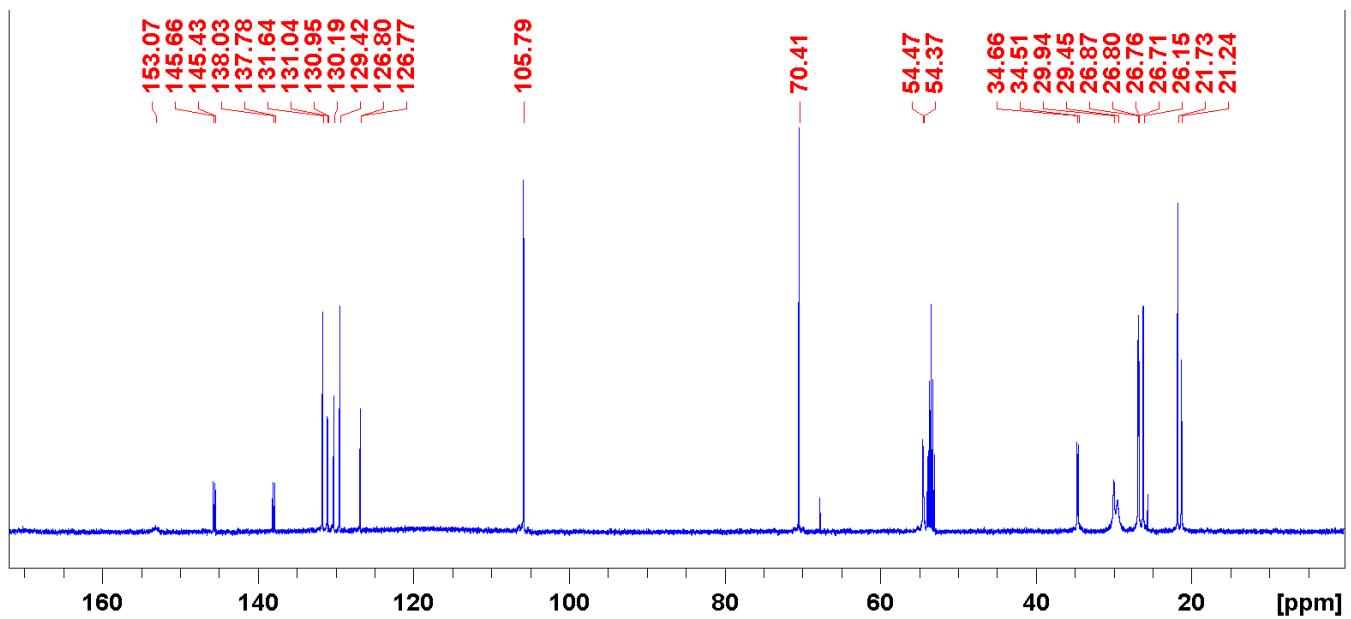


Figure S40. ^{13}C NMR spectrum (125 MHz; CD_2Cl_2) of **7**.

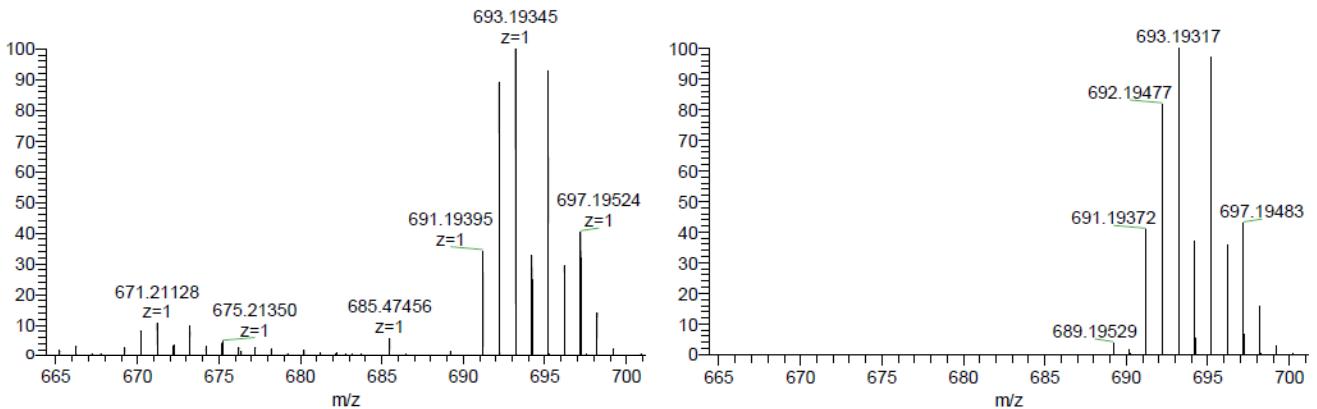
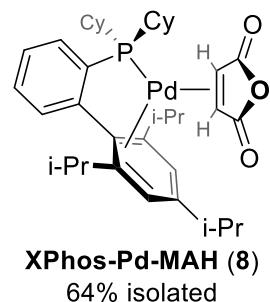


Figure S41. *Left:* Experimental HRMS-ESI spectrum of $[7 \bullet \text{Na}]^+$. *Right:* Calculated isotope pattern for $[7 \bullet \text{Na}]^+$.

XPhos-Pd-MAH (8)

Prepared according to the general procedure using **1** (109.9 mg, 0.2344 mmol), XPhos (112.9 mg, 0.2367 mmol), and THF (10 mL). Trituration/decantation 6 x with hexanes (4 mL). Yellow solid: 101.6 mg (64%). Crystals for X-ray diffraction were grown at room temperature from DCM/Et₂O (Et₂O as anti-solvent) by layering Et₂O on top of a concentrated solution of **8** in DCM. ^1H NMR: (500 MHz, CD_2Cl_2) δ 0.93 (d, 6H, $J = 6.3$ Hz, $-\text{CH}(\text{CH}_3)_2$), 1.16-1.52 (m, 10 H, Cy-H), 1.36 (d, 6H, $J = 6.7$ Hz, $-\text{CH}(\text{CH}_3)_2$), 1.43 (d, 6H, $J = 6.4$ Hz, $-\text{CH}(\text{CH}_3)_2$), 1.50-1.70 (br m, 6H, Cy-H), 1.87 (br m, 2H, Cy-H), 2.00-2.30 (br m, 6H, 2 x $-\text{CH}(\text{CH}_3)_2 + \text{Cy}-\text{H}$), 3.15 (sept, 1 H, $J = 6.9$ Hz, $-\text{CH}(\text{CH}_3)_2$), 4.48 (br s, 1H, $-\text{CH}=\text{CH}-$), 6.97 (br dd, 1H, $J = 2.8$ Hz, 7.1 Hz, Ar-H), 7.39 (br s, 2H, Ar-H), 7.43 (t, 1H, $J = 7.4$ Hz, Ar-H), 7.48 (t, 1H, $J = 7.4$ Hz, Ar-H), 7.68 (t, 1H, $J = 6.0$ Hz, Ar-H); $^{13}\text{C}\{\text{H}\}$ NMR: 23.8, 24.0, 24.9, 26.0, 27.0 (d, $J = 3.0$ Hz), 27.3 (d, $J = 3.0$ Hz), 29.2, 30.3, 31.5, 33.8, 36.3 (d, $J = 17.7$ Hz), 55.4, 122.7 (d, $J = 5.3$ Hz), 127.5 (d, $J = 3.6$ Hz), 129.9, 132.0, 132.2 (d, $J = 10.2$ Hz), 137.4 (d, $J = 29.1$ Hz), 146.7 (d, $J = 29.2$ Hz), 148.8; $^{31}\text{P}\{\text{H}\}$ NMR: 38.6. HRMS (ESI) of $[\text{C}_{37}\text{H}_{51}\text{O}_3\text{PPd} \bullet \text{H}]^+$ (major isotopomer, H^+ adduct): 681.26834 (calc'd); 681.26863 (found). Elemental analysis (CH) of $\text{C}_{37}\text{H}_{51}\text{O}_3\text{PPd}$: 65.24, 7.55 (calc'd); 65.30, 7.85 (actual).



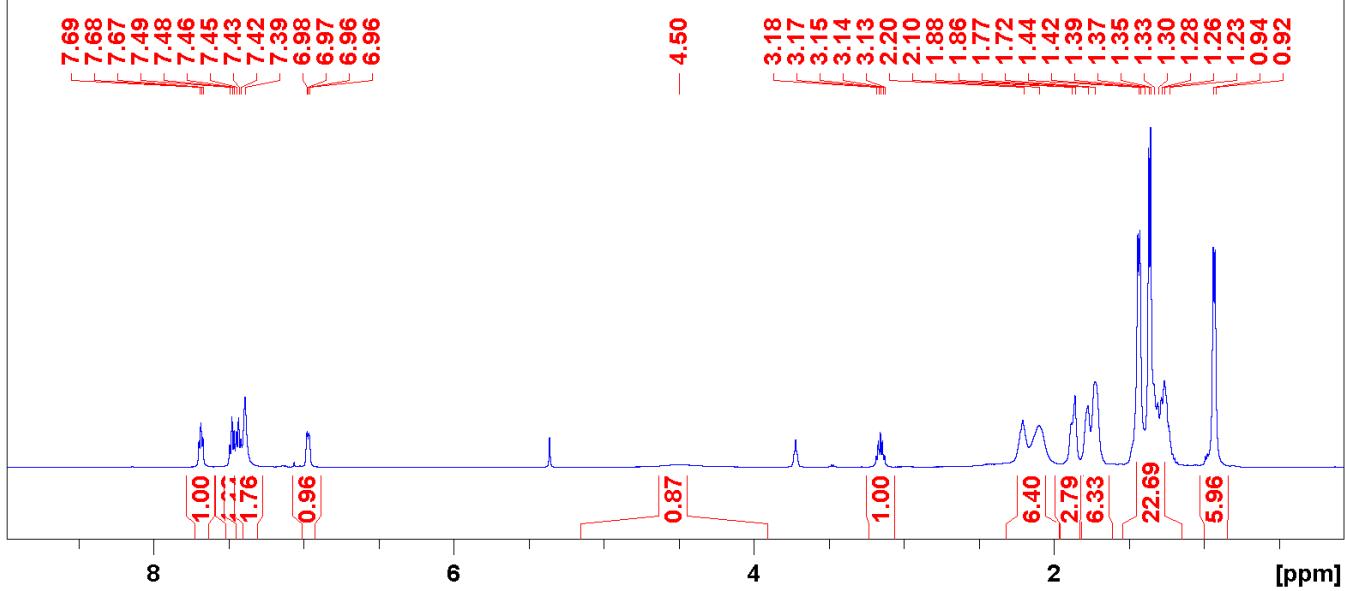


Figure S42. ¹H NMR spectrum (500 MHz; CD_2Cl_2) of **8**.

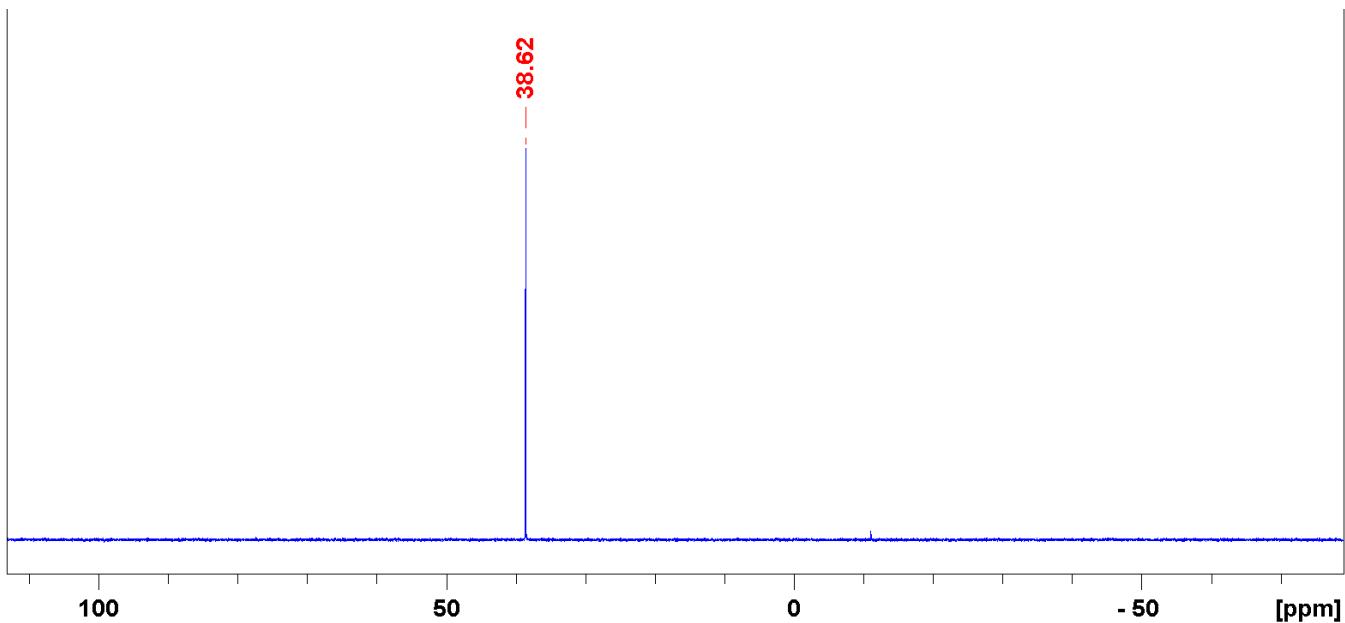


Figure S43. ³¹P NMR spectrum (202 MHz; CD_2Cl_2) of **8**.

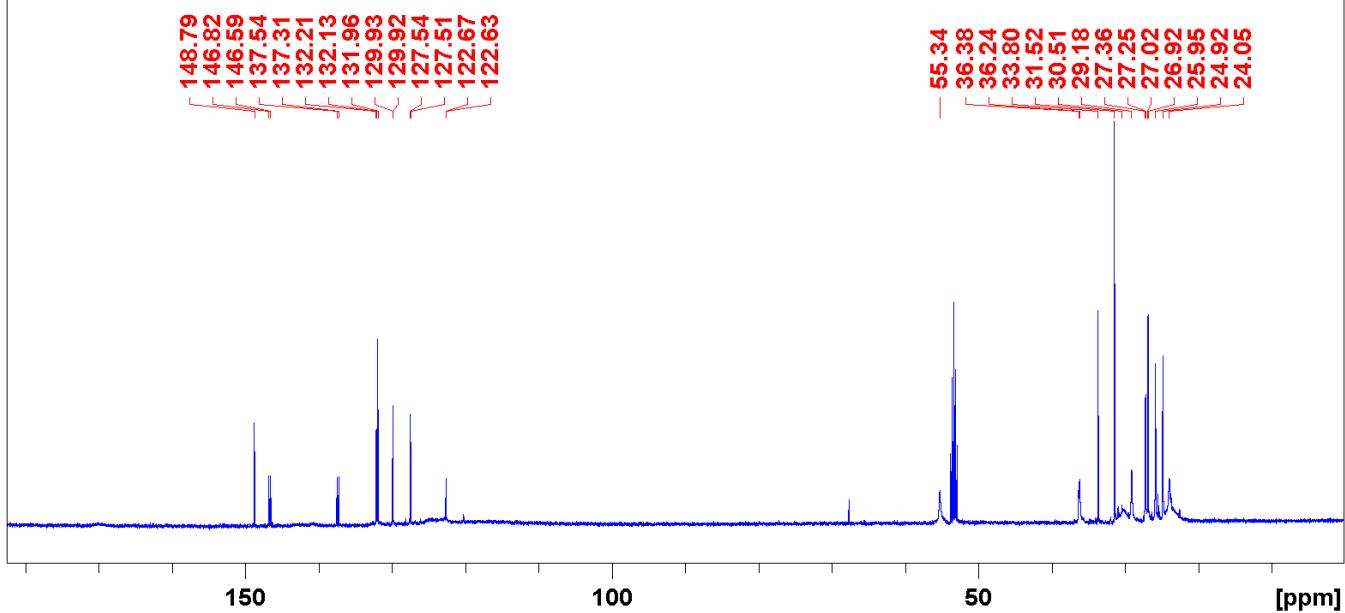


Figure S44. ¹³C NMR spectrum (125 MHz; CD₂Cl₂) of **8**.

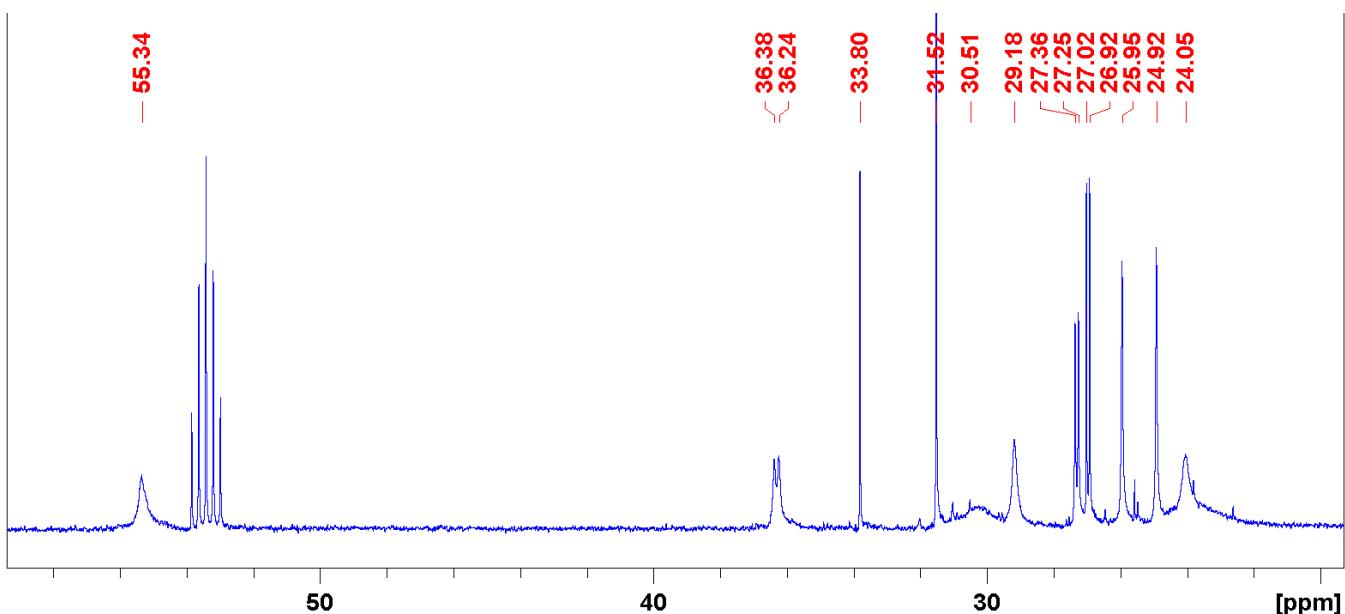


Figure S45. ¹³C NMR spectrum (125 MHz; CD₂Cl₂) of **8**. Expansion of aliphatic region.

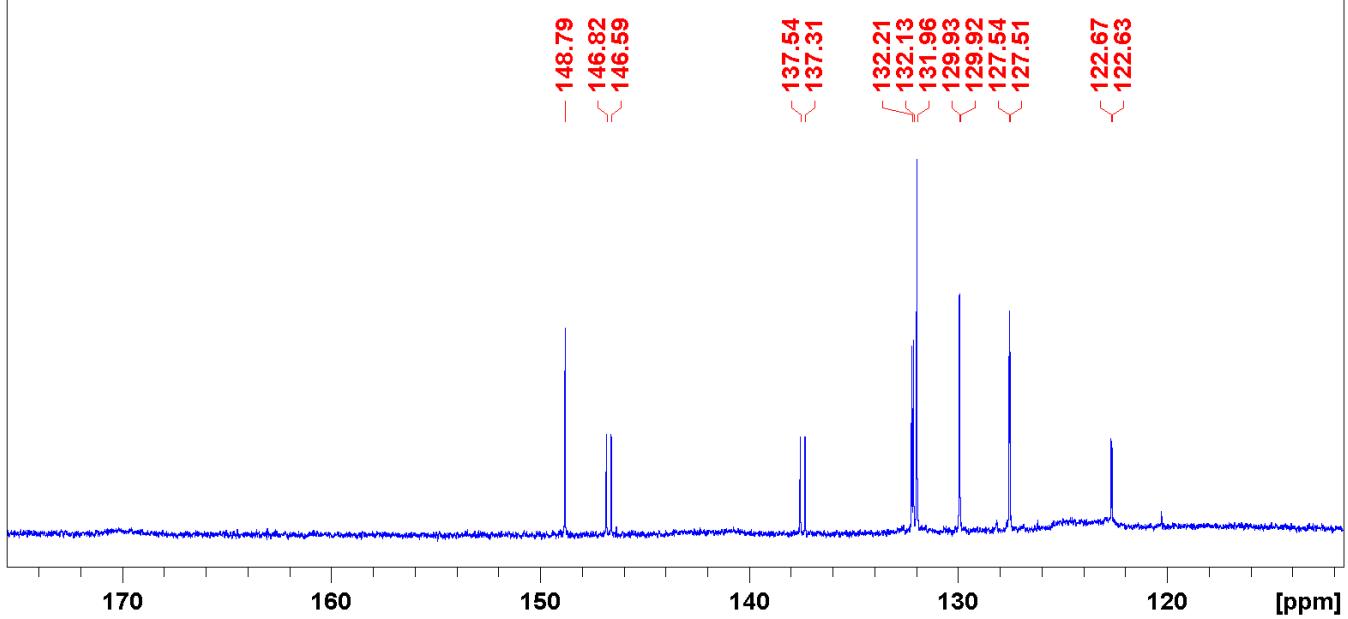


Figure S46. ^{13}C NMR spectrum (125 MHz; CD_2Cl_2) of **8**. Expansion of aromatic region.

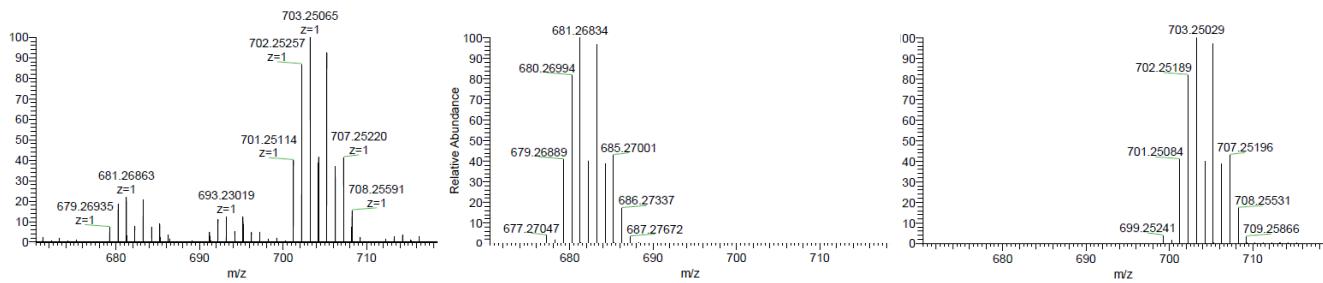


Figure S47. *Left:* Experimental HRMS-ESI spectrum of $[8\bullet\text{H}]^+$ and $[8\bullet\text{Na}]^+$. *Middle:* Calculated HRMS isotope pattern for $[8\bullet\text{H}]^+$. *Right:* Calculated HRMS isotope pattern for $[8\bullet\text{Na}]^+$.

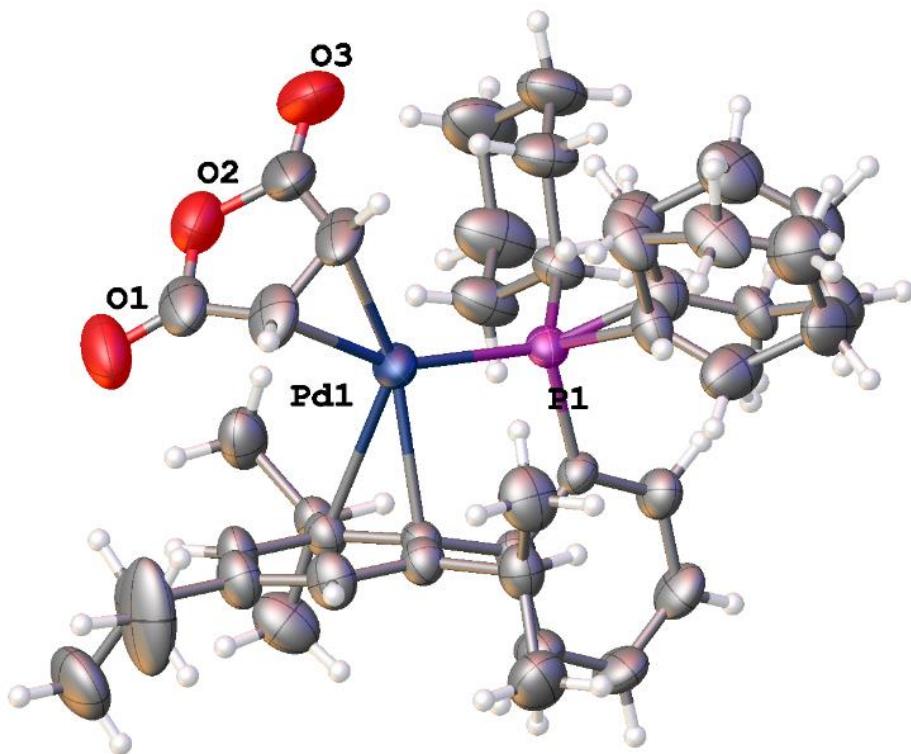
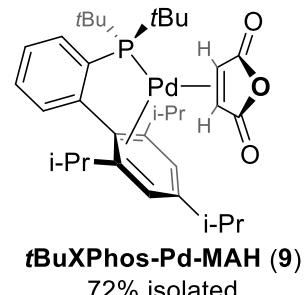


Figure S48. Solid-state molecular structure of complex **8**. Thermal ellipsoids plotted at 50% probability for non-H atoms; H-atoms are shown as uniformly-sized white spheres. One cyclohexyl is disordered between two conformations, both of which have half-occupancy. Selected bond lengths (\AA) and angles ($^\circ$): Pd1–P1: 2.2995(9); Pd1–C1: 2.077(3); Pd1–C2: 2.135(3); Pd1–C23: 2.369(3); P1–Pd1–C23: 83.84(7); P1–Pd1–C1: 115.45(13); C2–Pd1–C23: 120.86(14).

tBuXPhos–Pd–MAH (9)

Prepared according to the general procedure using **1** (100.0 mg, 0.2133 mmol), tBuXPhos (95.1 mg, 0.2240 mmol), and THF (5 mL). Trituration/decantation 3 x with diethyl ether (4 mL). Yellow solid: 97.0 mg (72%). ^1H NMR: (500 MHz, CDCl_3) δ 0.89 (d, 6H, J = 6.6 Hz, $-\text{CH}(\text{CH}_3)_2$), 1.33 (d, 6H, J = 6.6 Hz, $-\text{CH}(\text{CH}_3)_2$), 1.38 (d, 18H, J = 13.9 Hz, 2 x tBu), 1.42 (d, 6H, J = 7.6 Hz, $-\text{CH}(\text{CH}_3)_2$), 2.30 (sept, 2H, J = 7.0 Hz, 2 x $-\text{CH}(\text{CH}_3)_2$), 3.20 (sept, 1H, J = 7.2 Hz, $-\text{CH}(\text{CH}_3)_2$), 4.30 (br s, 1H, $-\text{CH}=\text{CH}-$), 7.00 (m, 1H, Ar–H), 7.37 (br s, 2H, Ar–H), 7.40–7.45 (m, 2H, Ar–H), 7.85 (m, 1H, Ar–H); $^{13}\text{C}\{\text{H}\}$ NMR: 24.3 (br), 25.9, 31.0 (m), 31.3 (br), 33.6, 36.5 (br), 56.8 (d, J = 13.3 Hz), 122.6 (d, J = 5.0 Hz), 126.9, 127.0, 129.7 (d, J = 2.1 Hz), 133.3 (d, J = 10.4 Hz), 134.7, 137.7 (d, J = 19.5 Hz), 147.9 (d, J = 29.2 Hz), 149.2, 170.0 (v br); $^{31}\text{P}\{\text{H}\}$ NMR: 65.6. HRMS (ESI) of $[\text{C}_{33}\text{H}_{47}\text{O}_3\text{PPd}\bullet\text{H}]^+$ (major isotopomer, H^+ adduct): 629.23704 (calc'd); 629.23715 (found). Elemental analysis (CH) of $\text{C}_{33}\text{H}_{47}\text{O}_3\text{PPd}$: 63.00, 7.53 (calc'd); 62.43, 7.45 (actual).



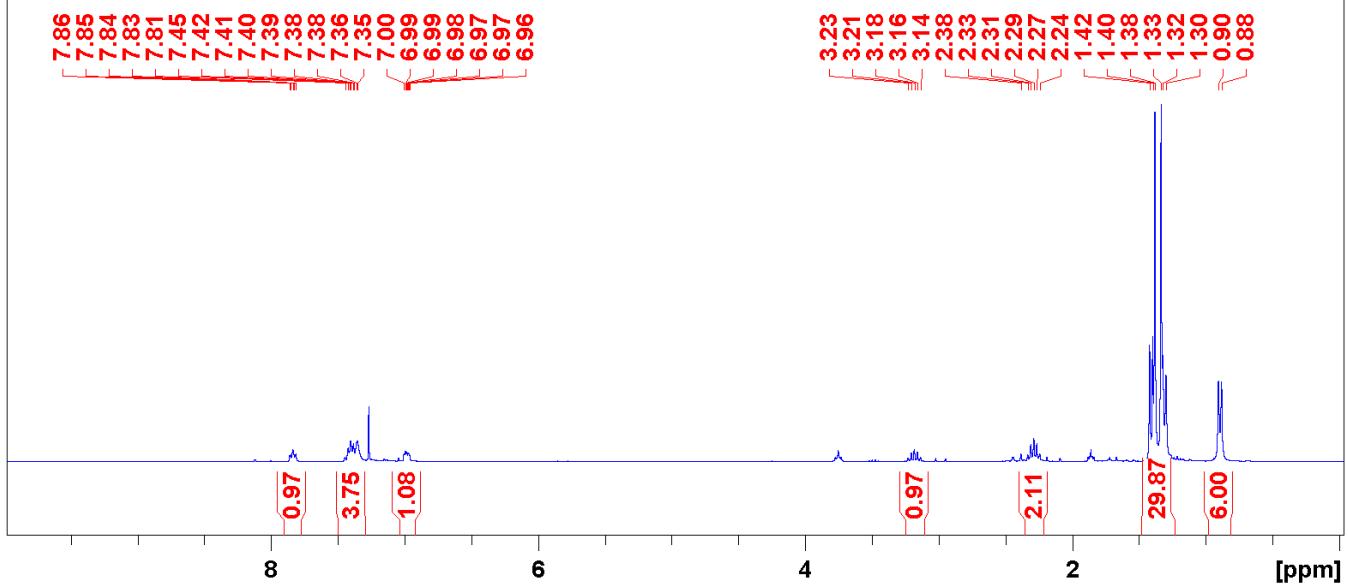


Figure S49. ^1H NMR spectrum (500 MHz; CDCl_3) of 9.

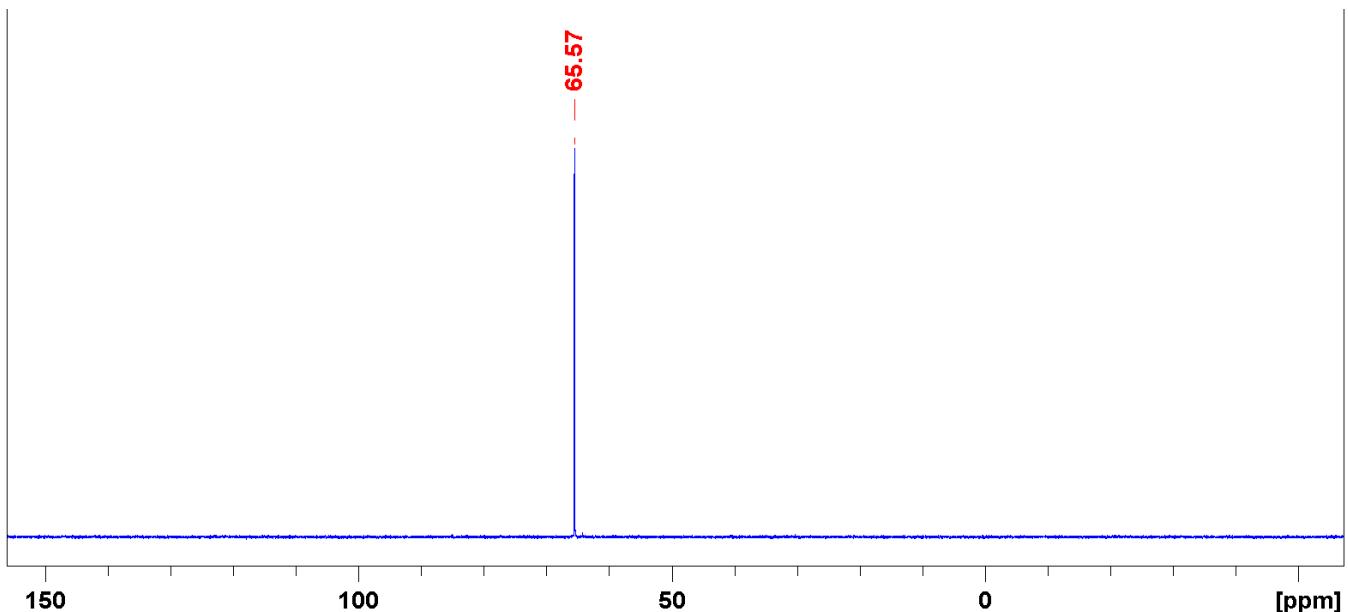


Figure S50. ^{31}P NMR spectrum (202 MHz; CDCl_3) of 9.

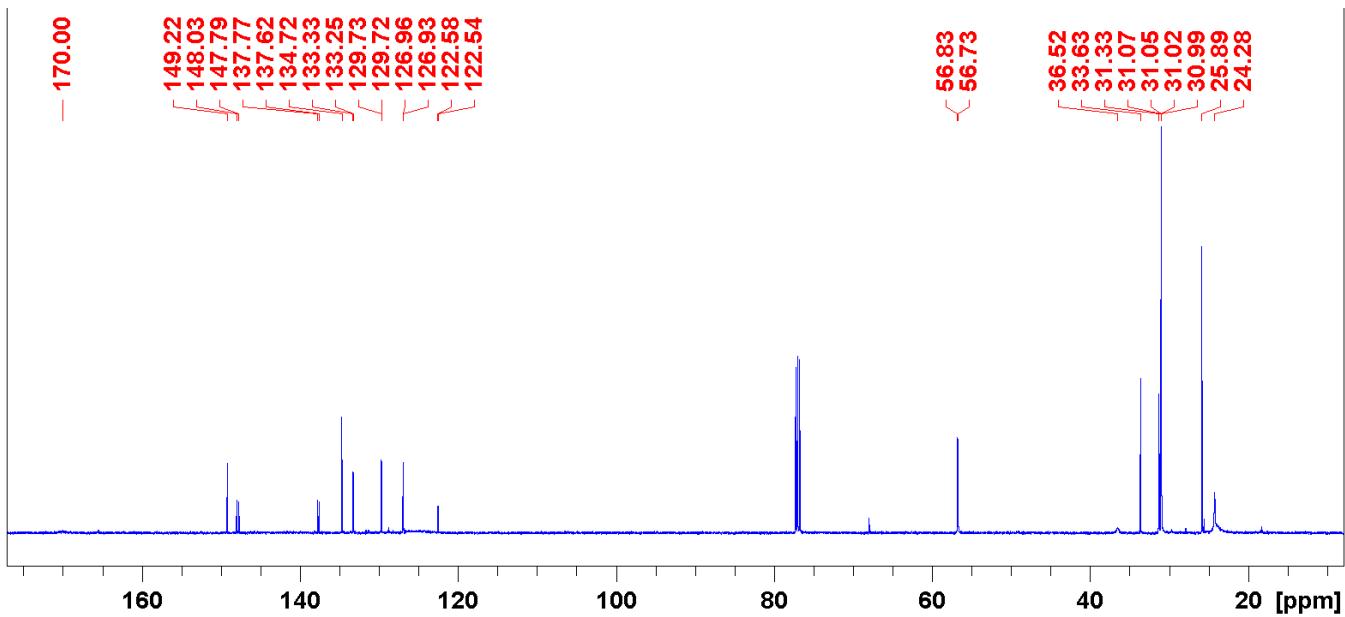


Figure S51. ¹³C NMR spectrum (125 MHz; CDCl₃) of **9**.

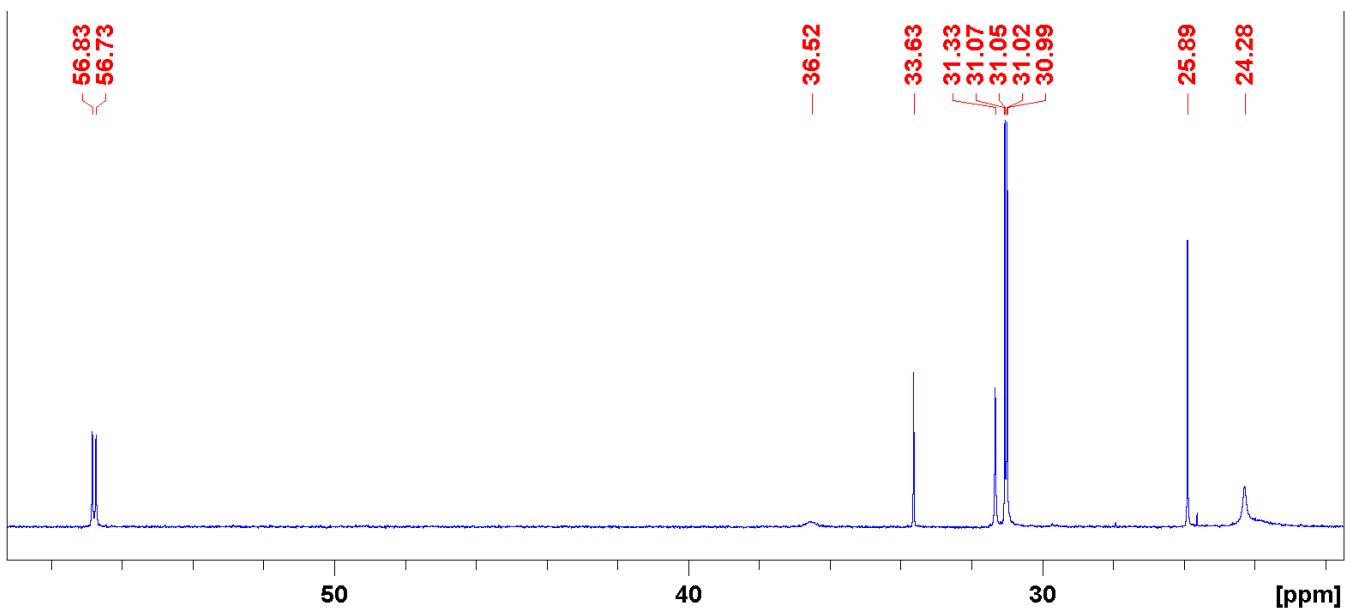


Figure S52. ¹³C NMR spectrum (125 MHz; CDCl₃) of **9**. Expansion of aliphatic region.

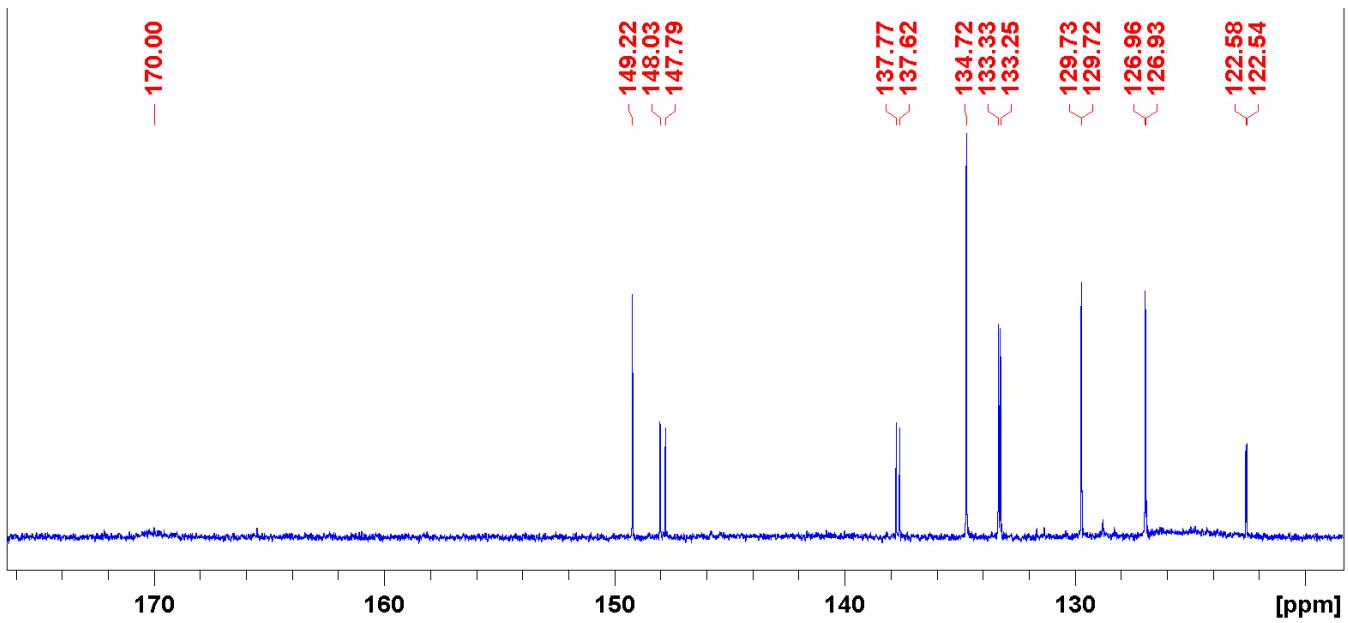


Figure S53. ^{13}C NMR spectrum (125 MHz; CDCl_3) of **9**. Expansion of aromatic region.

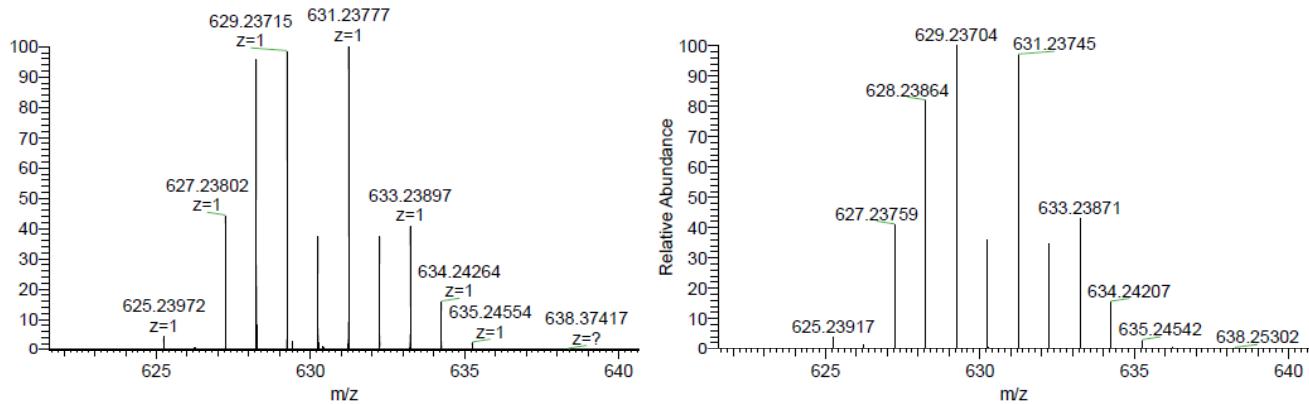
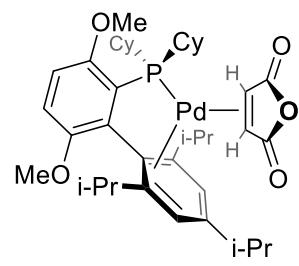


Figure S54. Left: Experimental HRMS-ESI spectrum of $[9\bullet\text{H}]^+$. Right: Calculated HRMS isotope pattern for $[9\bullet\text{H}]^+$.

BrettPhos–Pd–MAH (**10**)

Prepared according to the general procedure using **1** (91.0 mg, 0.1941 mmol), BrettPhos (104.2 mg, 0.1941 mmol), and THF (9 mL). Trituration/decantation 5 x with hexanes (5 mL). Yellow solid: 92.3 mg (64%). ^1H NMR: (500 MHz, CD_2Cl_2) δ 0.88 (br d, 6H, $J = 4.75$ Hz), 1.04-2.21 (m, 20H, Cy–H), 1.35 (br d, 6H, $J = 6.7$ Hz), 1.43 (br s, 6H), 2.28 (br s, 2H), 2.56 (br s, 2H), 3.13 (sept, 1H, $J = 6.7$ Hz), 3.46 (s, 3H), 3.90 (s, 3H), 4.45 (br s, 1H), 6.83-7.00 (m, 2H), 7.21-7.50 (m, 2H); $^{13}\text{C}\{\text{H}\}$ NMR: (125 MHz, CD_2Cl_2) δ 22.6, 22.8, 23.3, 23.6, 23.9, 24.4, 24.7, 25.0, 25.5, 26.1, 27.2 (d, $J = 15.4$ Hz), 27.5 (d, $J = 11.4$ Hz), 30.4, 31.2, 33.2, 33.8, 38.0 (d, $J = 130.5$ Hz), 54.5, 55.4, 55.8, 110.7 (d, $J = 3.1$ Hz), 113.0, 116.0 d ($J = 5.7$ Hz), 122.2, 124.9, 127.5 (d, $J = 23.5$ Hz), 137.3 (d, $J = 30.0$ Hz), 141.2, 145.4, 148.8, 152.2 (d, $J = 14.9$ Hz), 155.4 (d, $J = 2.5$ Hz), 169.4, 171.1; $^{31}\text{P}\{\text{H}\}$ NMR: (121 MHz, CD_2Cl_2) δ 46.0. HRMS (ESI) of $[\text{C}_{39}\text{H}_{55}\text{O}_5\text{PPd}\bullet\text{H}]^+$ (major isotopomer, H^+ adduct): 741.28947 (calc'd); 741.28956 (found). Elemental analysis (CH) of $\text{C}_{39}\text{H}_{55}\text{O}_5\text{PPd}$: 63.19, 7.48 (calc'd); 63.38, 7.72 (actual).



BrettPhos-Pd-MAH (10**)**
64% isolated

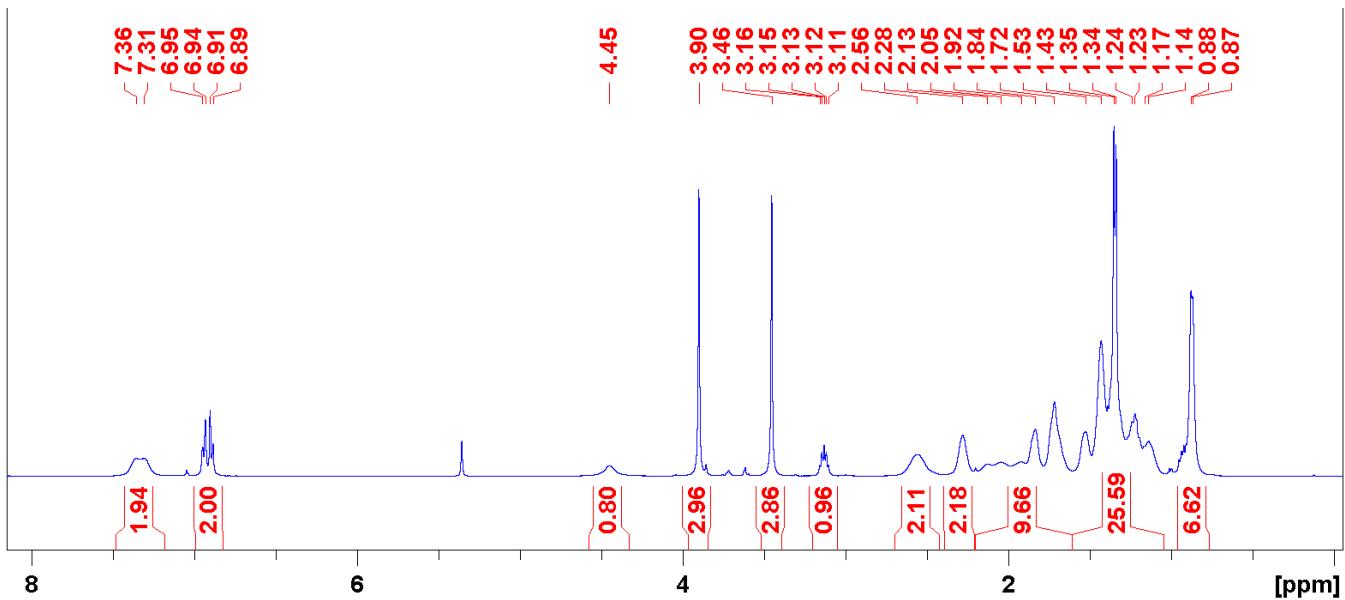


Figure S55. ^1H NMR spectrum (500 MHz; CD_2Cl_2) of **10**.

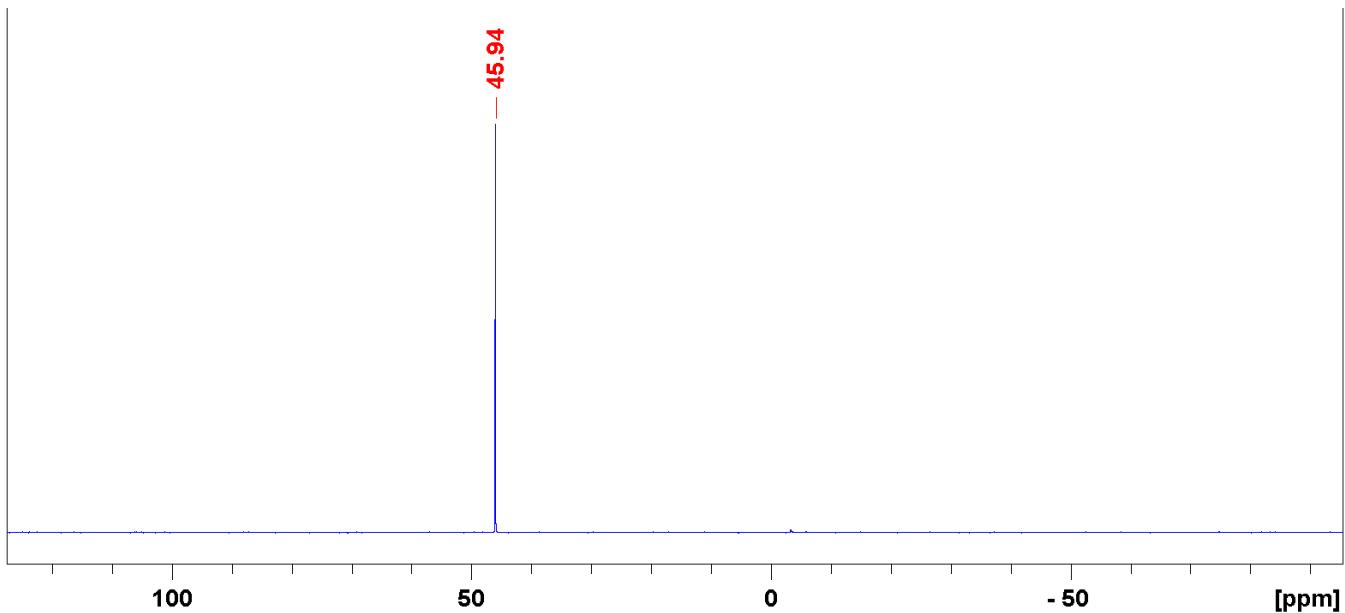


Figure S56. ^{31}P NMR spectrum (121 MHz; CD_2Cl_2) of **10**.

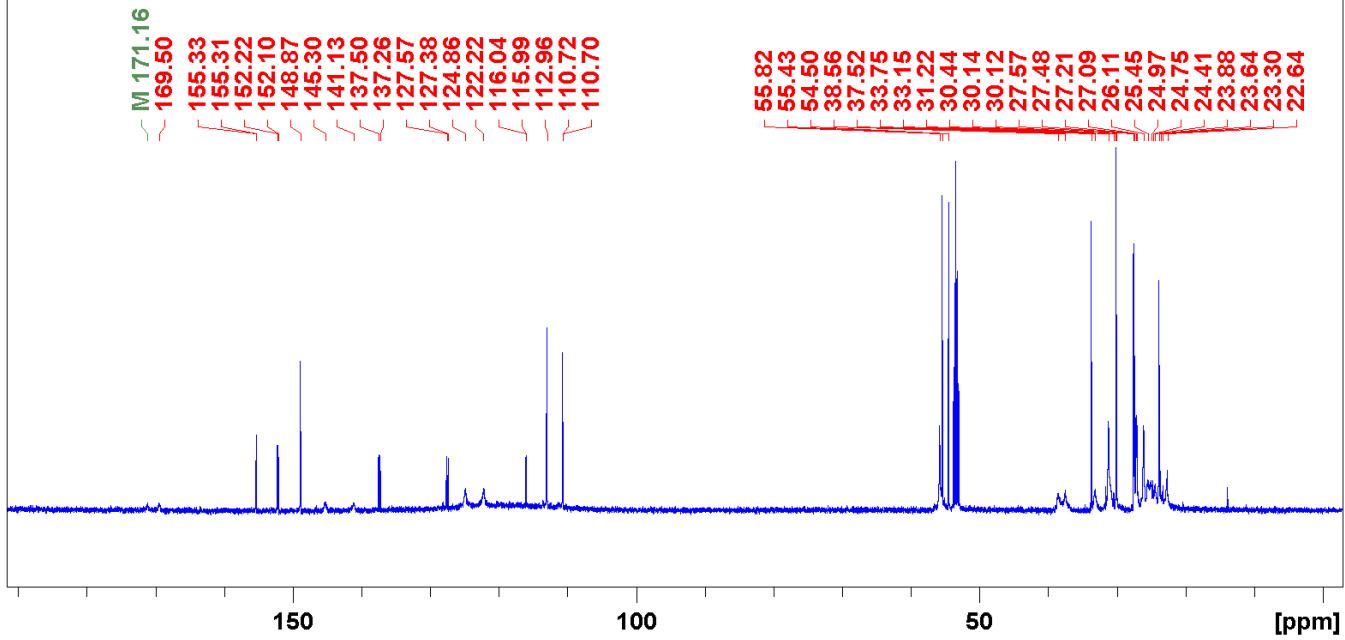


Figure S57. ^{13}C NMR spectrum (125 MHz; CD_2Cl_2) of **10**.

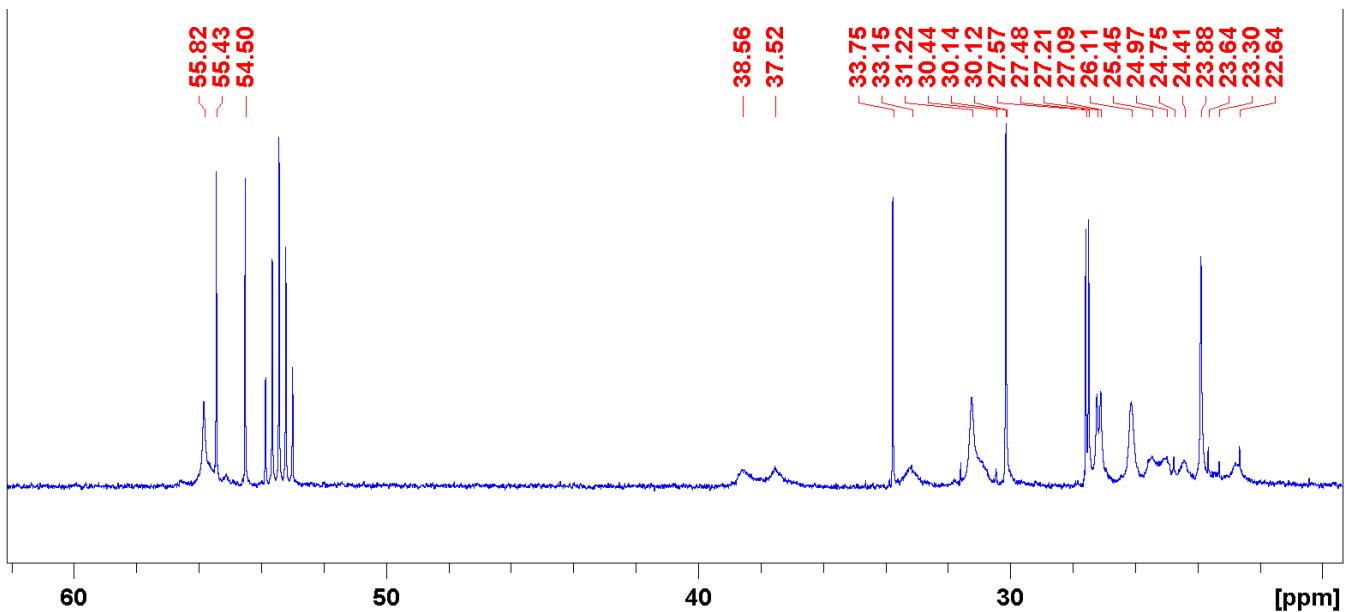


Figure S58. ^{13}C NMR spectrum (125 MHz; CD_2Cl_2) of **10**. Expansion of aliphatic region.

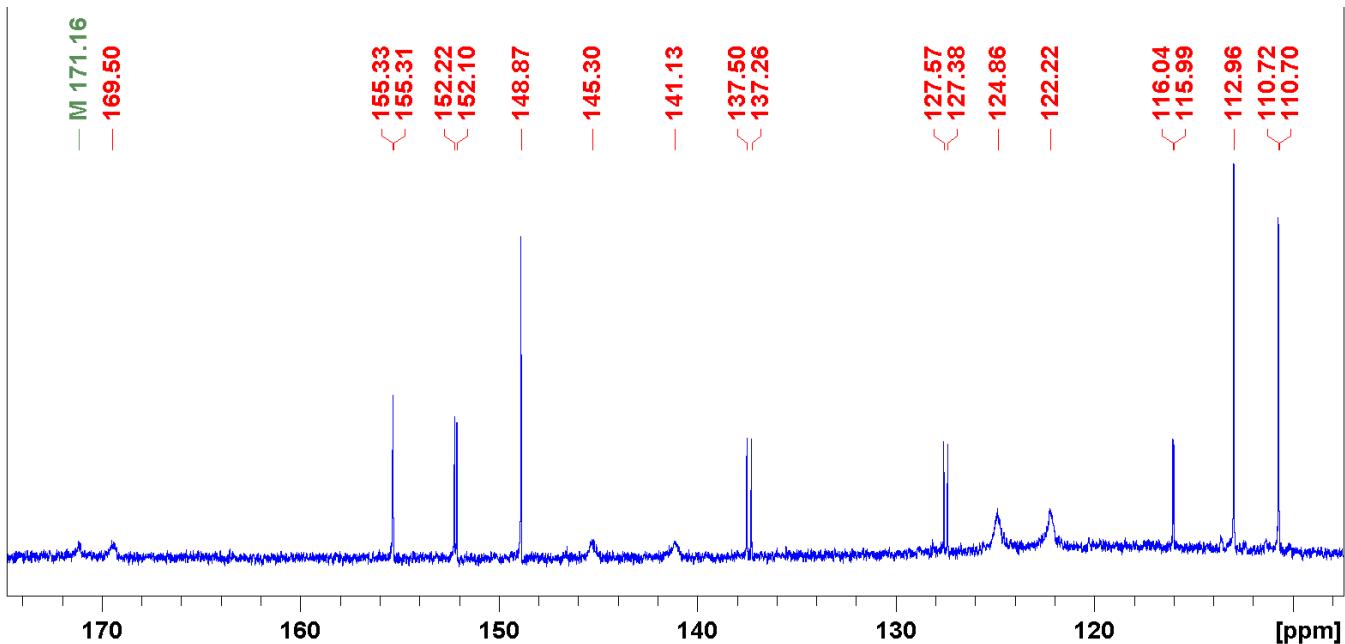


Figure S59. ^{13}C NMR spectrum (125 MHz; CD_2Cl_2) of **10**. Expansion of aromatic region.

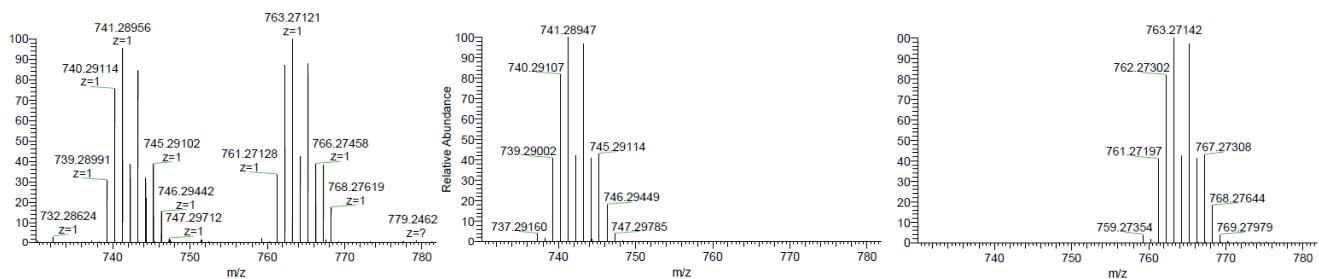
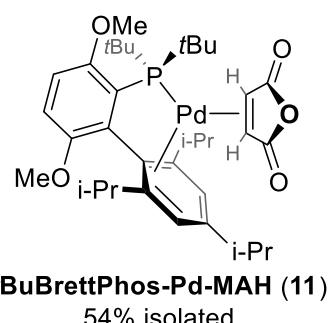


Figure S60. *Left:* Experimental HRMS-ESI spectrum of $[\mathbf{10} \bullet \text{H}]^+$ and $[\mathbf{10} \bullet \text{Na}]^+$. *Middle:* Calculated HRMS isotope pattern for $[\mathbf{10} \bullet \text{H}]^+$. *Right:* Calculated HRMS isotope pattern for $[\mathbf{10} \bullet \text{Na}]^+$.

*t*BuBrettPhos-Pd-MAH (11)

Prepared according to the general procedure using **1** (56.0 mg, 0.1194 mmol), *t*BuBrettPhos (60.8 mg, 0.1254 mmol), and THF (2.5 mL). Trituration/decantation 5 x with hexanes (5 mL). Yellow solid: 44.0 mg (54%). ^1H NMR: (300 MHz, CDCl_3) δ 0.88 (br m, 6H), 1.20–1.50 (br m, 30H), 2.01 (br m, 1H, $-\text{CH}=\text{CH}-$), 3.15 (sept, 1H, J = 6.8 Hz), 3.41 (s, 3H), 3.84 (s, 3H), 4.27 (br s, 1H, $-\text{CH}=\text{CH}-$), 6.85 (d, 1H, J = 8.7 Hz), 6.93 (dd, 1H, J = 1.8, 8.8 Hz), 7.19 (br s, 1H), 7.42 (br s, 1H); $^{13}\text{C}\{\text{H}\}$ NMR: (500 MHz, CDCl_3) δ 23.1 (br), 24.7, 25.3 (br), 31.4 (br), 31.8 (d, J = 7.8 Hz), 33.7, 54.1, 54.3, 57.6, 57.7, 110.3 (d, J = 2.7 Hz), 112.9 (d, J = 1.2 Hz), 114.7 (d, J = 5.3 Hz), 122.5 (br), 126.4 (br), 128.6 (d, J = 11.2 Hz), 139.1 (d, J = 30.5 Hz), 149.3, 152.0 (d, J = 15.2 Hz), 154.7 (d, J = 2.1 Hz); $^{31}\text{P}\{\text{H}\}$ NMR: (300 MHz, CD_2Cl_2) δ 72.1. HRMS (ESI) of $[\text{C}_{35}\text{H}_{51}\text{O}_5\text{PPd} \bullet \text{H}]^+$ (major isotopomer, H^+ adduct): 689.25817 (calc'd); 689.25851 (found). Elemental analysis (CH) of $\text{C}_{35}\text{H}_{51}\text{O}_5\text{PPd}$: 61.00, 7.46 (calc'd); 60.98, 7.35 (actual).



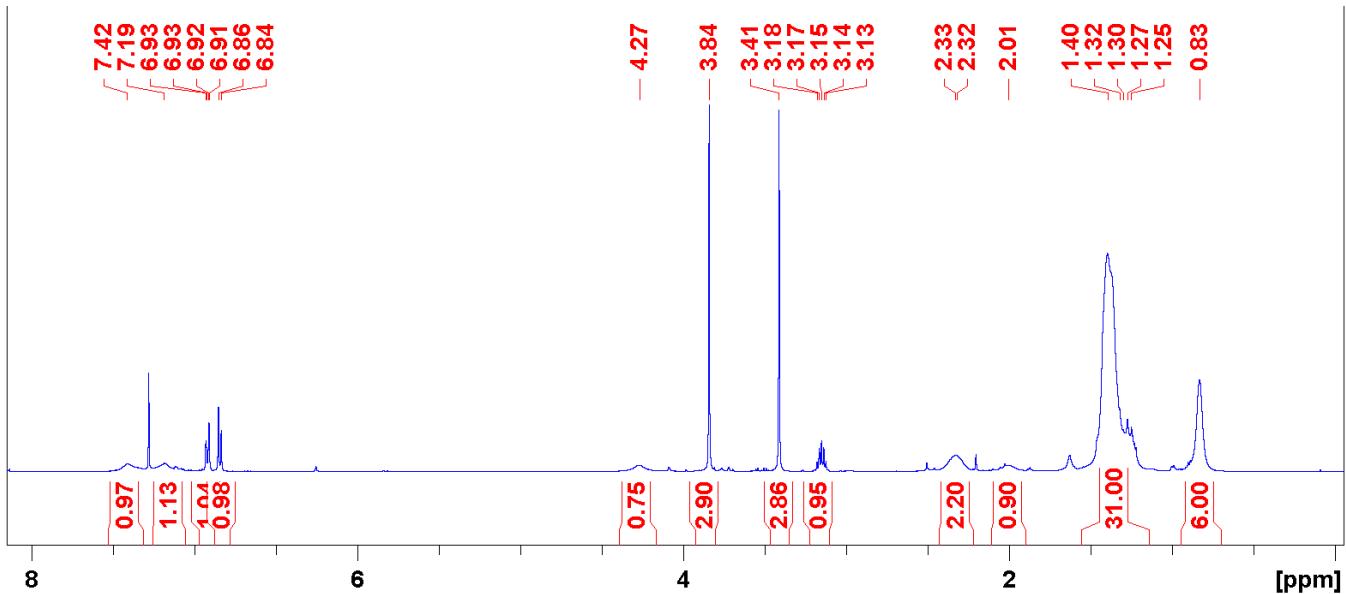


Figure S61. ^1H NMR spectrum (500 MHz; CDCl_3) of **11**.

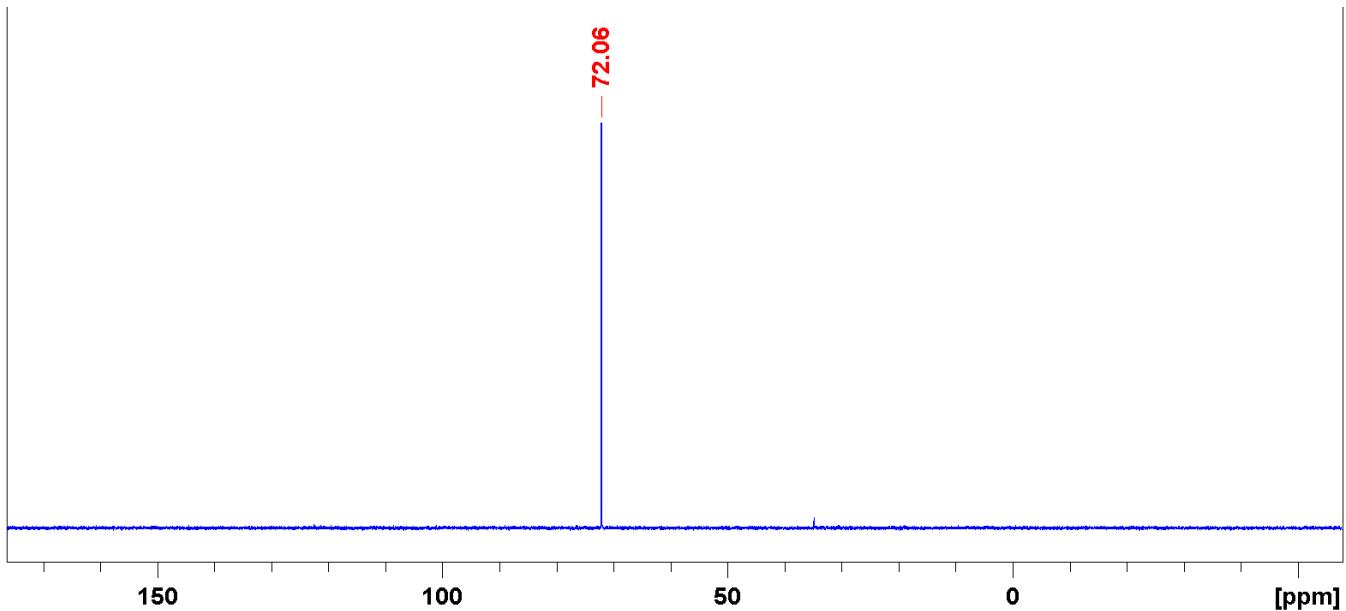


Figure S62. ^{31}P NMR spectrum (121 MHz; CDCl_3) of **11**.

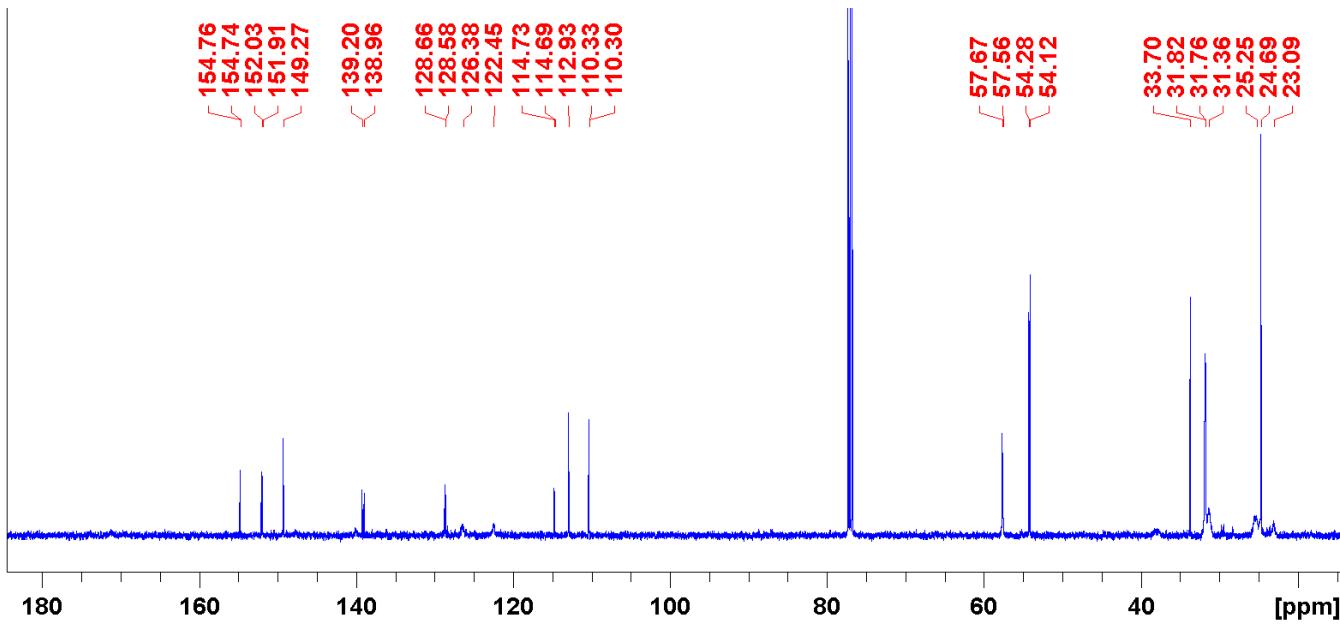


Figure S63. ¹³C NMR spectrum (125 MHz; CDCl₃) of **11**.

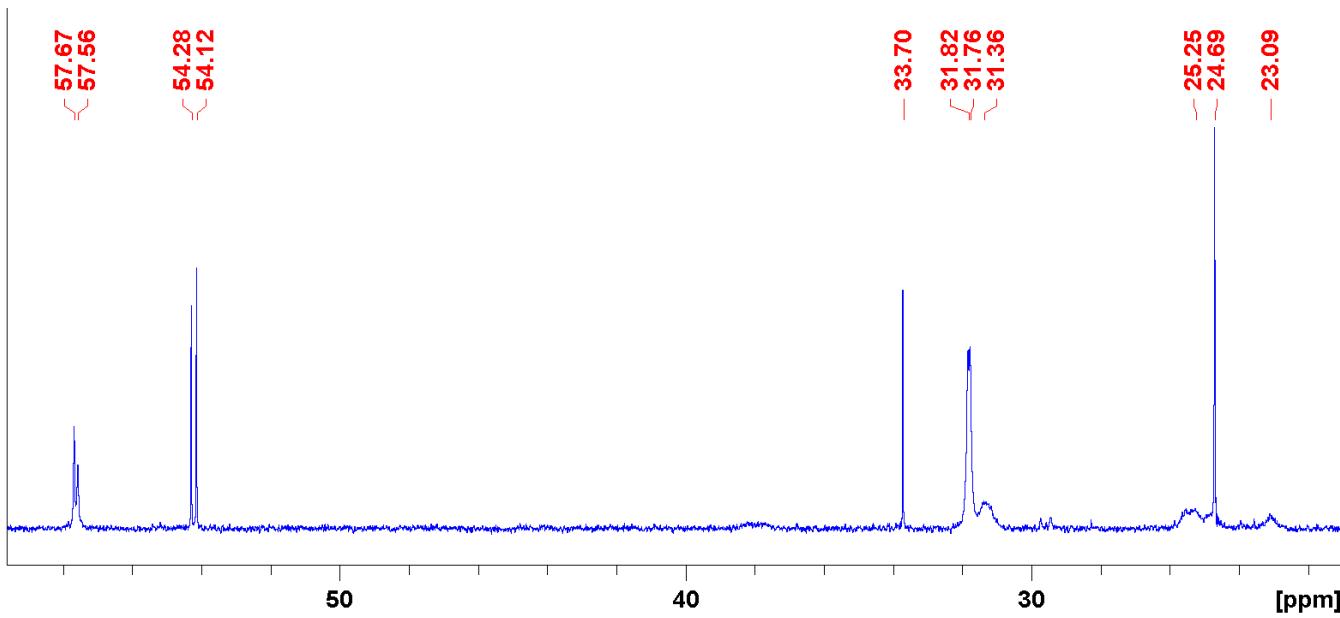


Figure S64. ¹³C NMR spectrum (125 MHz; CDCl₃) of **11**. Expansion of aliphatic region.

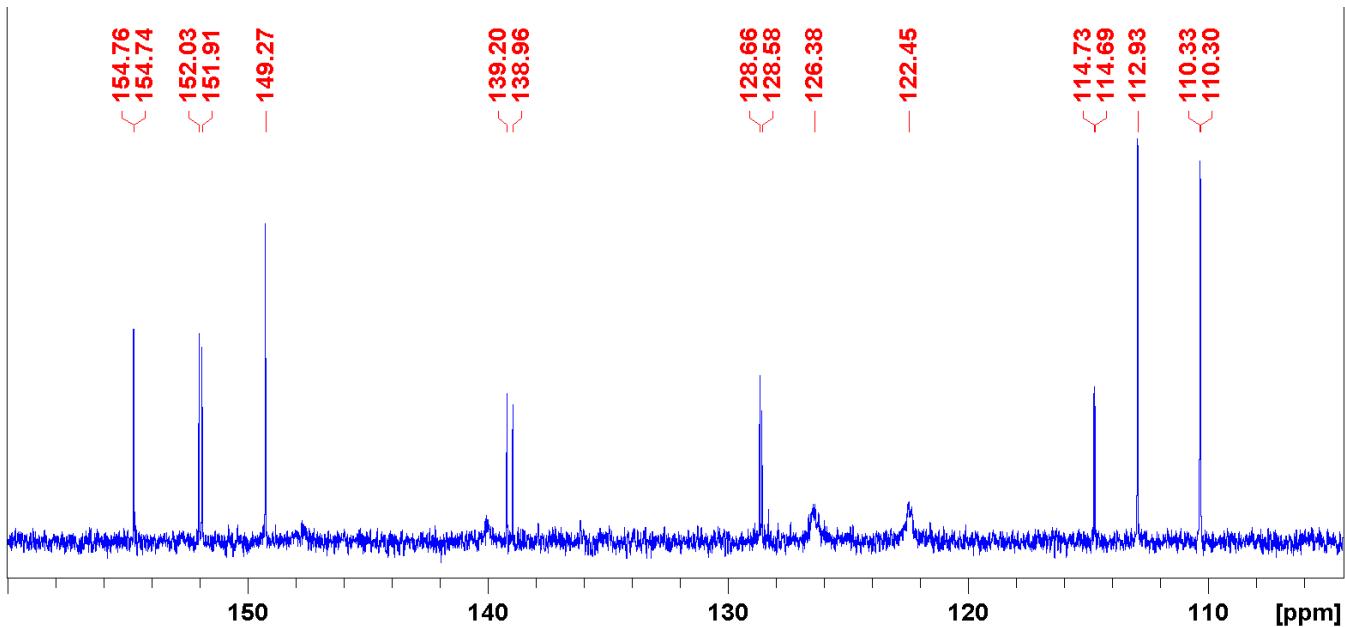


Figure S65. ^{13}C NMR spectrum (125 MHz; CDCl_3) of **11**. Expansion of aromatic region.

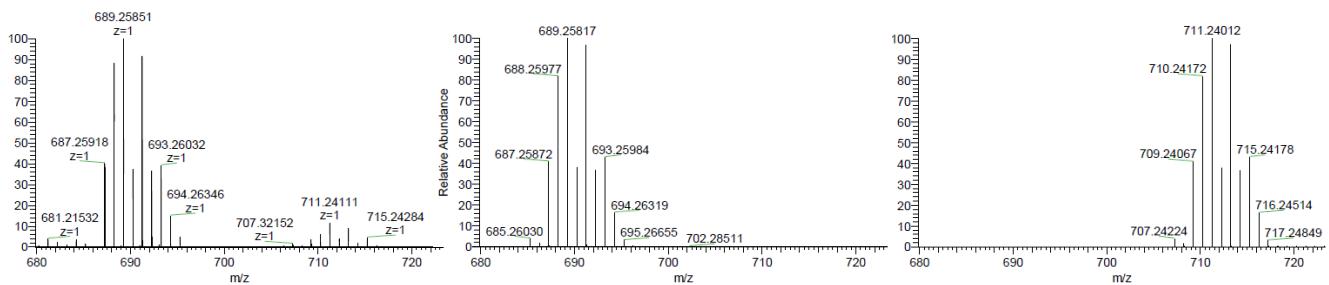
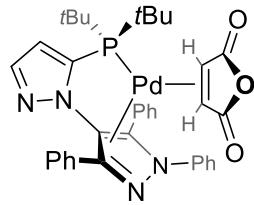


Figure S66. *Left:* Experimental HRMS-ESI spectrum of $[\mathbf{11} \bullet \text{H}]^+$ and $[\mathbf{11} \bullet \text{Na}]^+$. *Middle:* Calculated HRMS isotope pattern for $[\mathbf{11} \bullet \text{H}]^+$. *Right:* Calculated HRMS isotope pattern for $[\mathbf{11} \bullet \text{Na}]^+$.

BippyPhos-Pd-MAH (12)

Prepared according to the general procedure using **1** (100.0 mg, 0.2133 mmol), BippyPhos (113.5 mg, 0.2240 mmol), and THF (5 mL). Trituration/decantation 5 x with hexanes (5 mL). Tan solid: 130.0 mg (86%). ^1H NMR: (300 MHz, CDCl_3) δ 0.73 (d, 9H, $J = 15.0$ Hz), 0.87 (d, 9H, $J = 15.3$ Hz), 3.98 (dd, 1H, $J = 4.2, 6.3$ Hz) 4.32 (d, 1H, $J = 4.1$ Hz), 6.60 (d, 1H, $J = 2.1$ Hz), 7.21-7.42 (m, 13H), 7.74 (m, 2H), 8.12 (d, 1H, $J = 1.9$ Hz); $^{13}\text{C}\{\text{H}\}$ NMR: (125 MHz, CD_2Cl_2) δ 28.7 (d, $J = 8.3$ Hz), 28.8 (d, $J = 8.3$ Hz), 34.5 (d, $J = 13.6$ Hz), 34.7 (d, $J = 13.3$ Hz), 51.3 (d, $J = 14.2$ Hz), 54.8 (d, $J = 2.2$ Hz), 107.7, 113.3, 125.9, 127.7, 127.8, 128.2, 128.6, 128.8, 128.9, 129.3, 139.0, 130.3, 130.8, 139.3, 140.8, 144.1 (d, $J = 29.3$ Hz), 144.4 (d, $J = 5.8$ Hz), 150.7, 169.2 (d, $J = 3.3$ Hz), 170.4; $^{31}\text{P}\{\text{H}\}$ NMR: (121 MHz, CDCl_3) δ 46.5. HRMS (ESI) of $[\text{C}_{36}\text{H}_{37}\text{N}_4\text{O}_3\text{PPd} \bullet \text{Na}]^+$ (major isotopomer, Na^+ adduct): 733.15303 (calc'd); 733.15292 (found). Elemental analysis (CHN) of $\text{C}_{36}\text{H}_{37}\text{N}_4\text{O}_3\text{PPd}$: 60.81, 5.24, 7.88 (calc'd); 60.57, 5.33, 7.86 (actual).



BippyPhos-Pd-MAH (12)
86% isolated

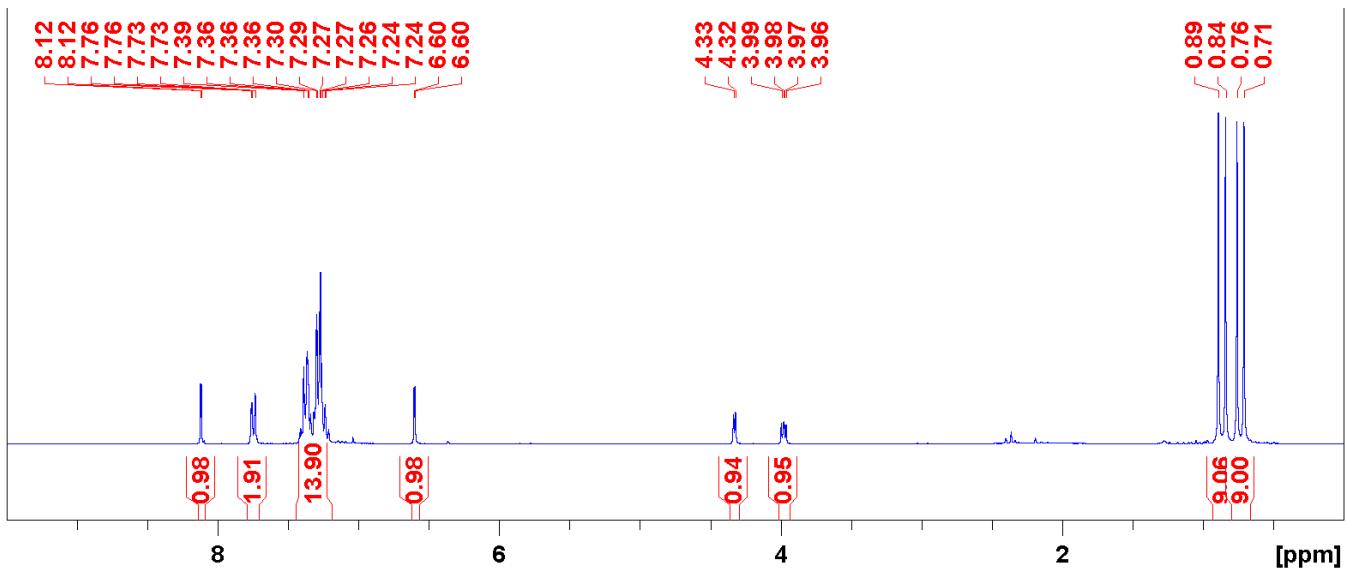


Figure S67. ^1H NMR spectrum (300 MHz; CDCl_3) of **12**.

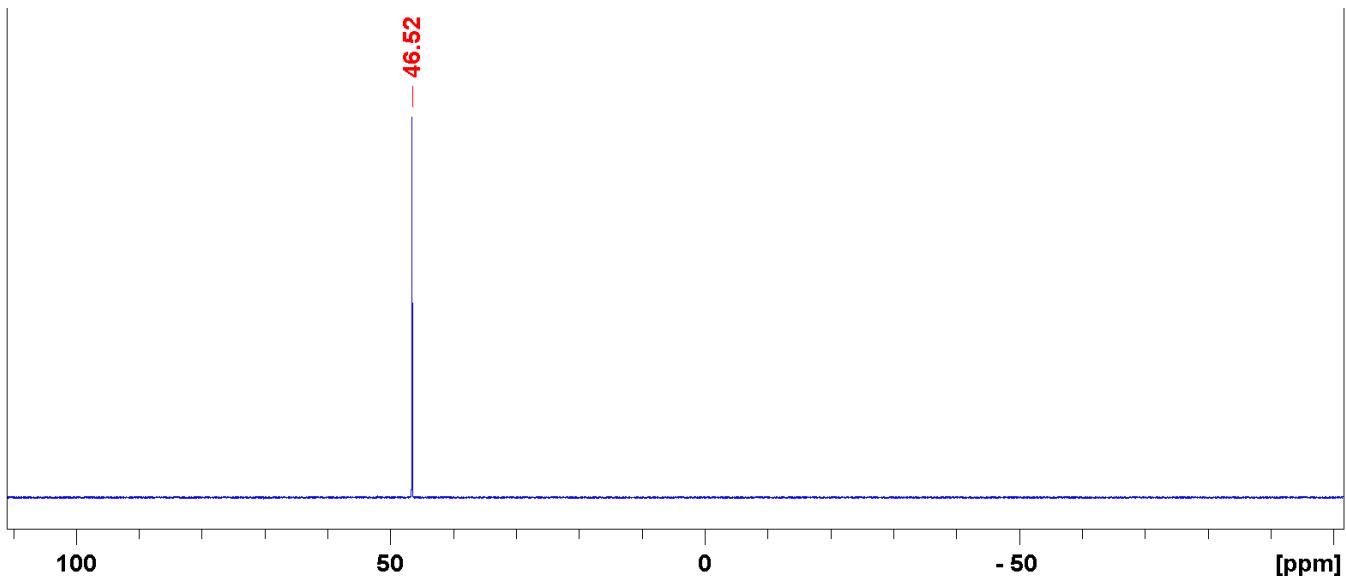


Figure S68. ^{31}P NMR spectrum (121 MHz; CDCl_3) of **12**.

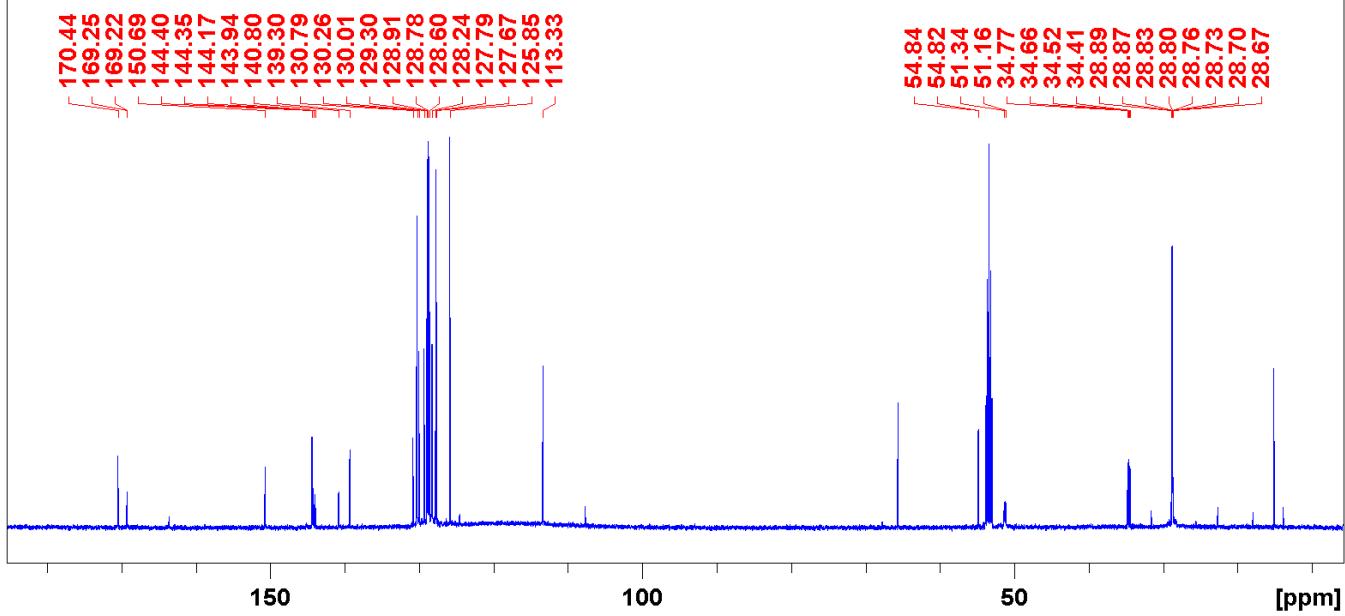


Figure S69. ¹³C NMR spectrum (125 MHz; CD₂Cl₂) of **12**.

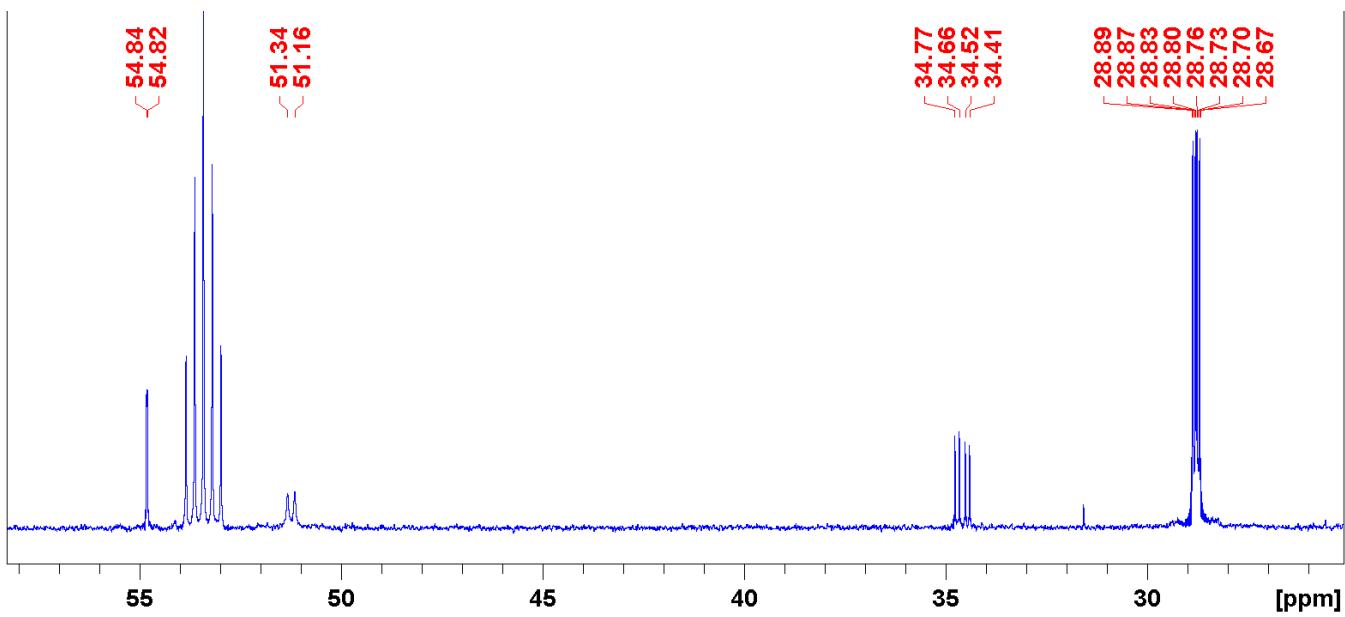


Figure S70. ¹³C NMR spectrum (125 MHz; CD₂Cl₂) of **12**. Expansion of aliphatic region.

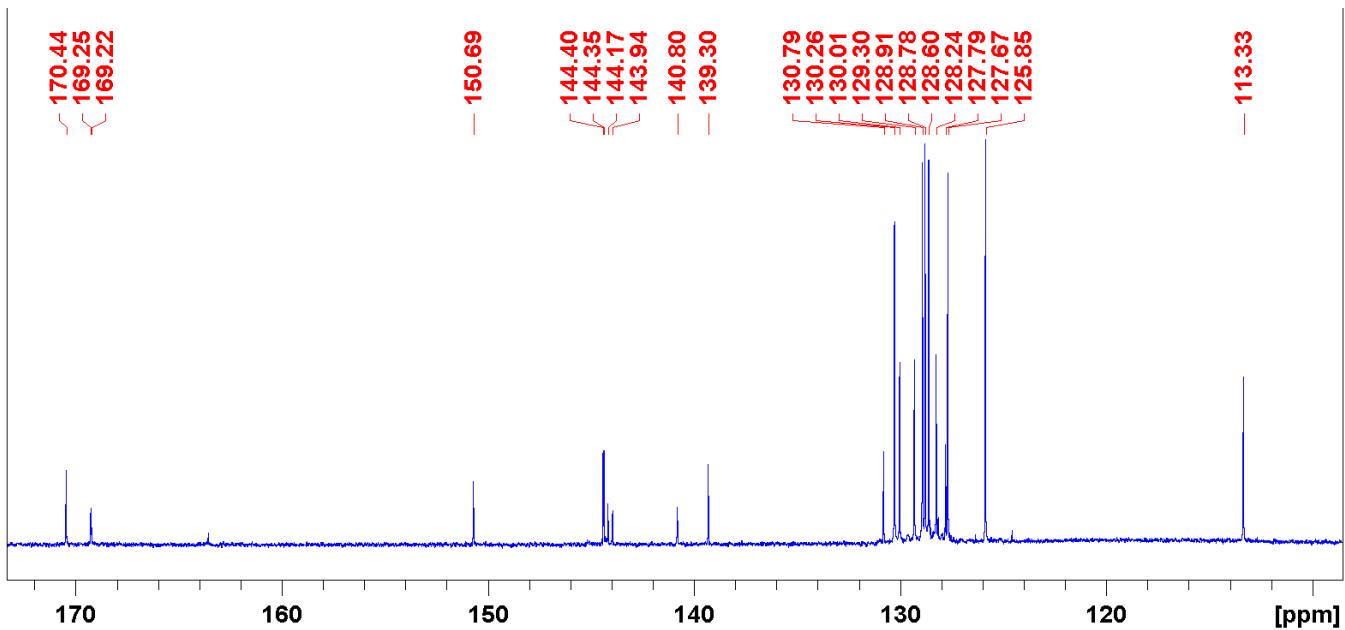


Figure S71. ^{13}C NMR spectrum (125 MHz; CD_2Cl_2) of **12**. Expansion of aromatic region.

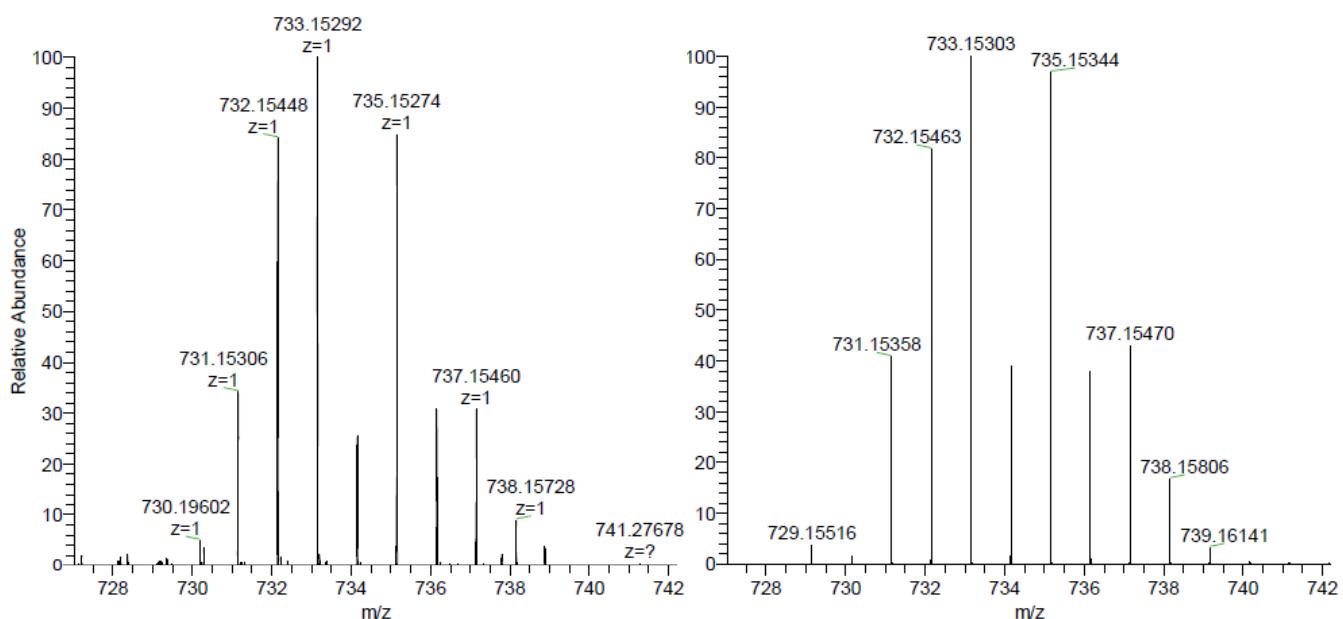


Figure S72. *Left:* Experimental HRMS-ESI spectrum of $[12 \bullet \text{H}]^+$. *Right:* Calculated HRMS isotope pattern for $[12 \bullet \text{H}]^+$.

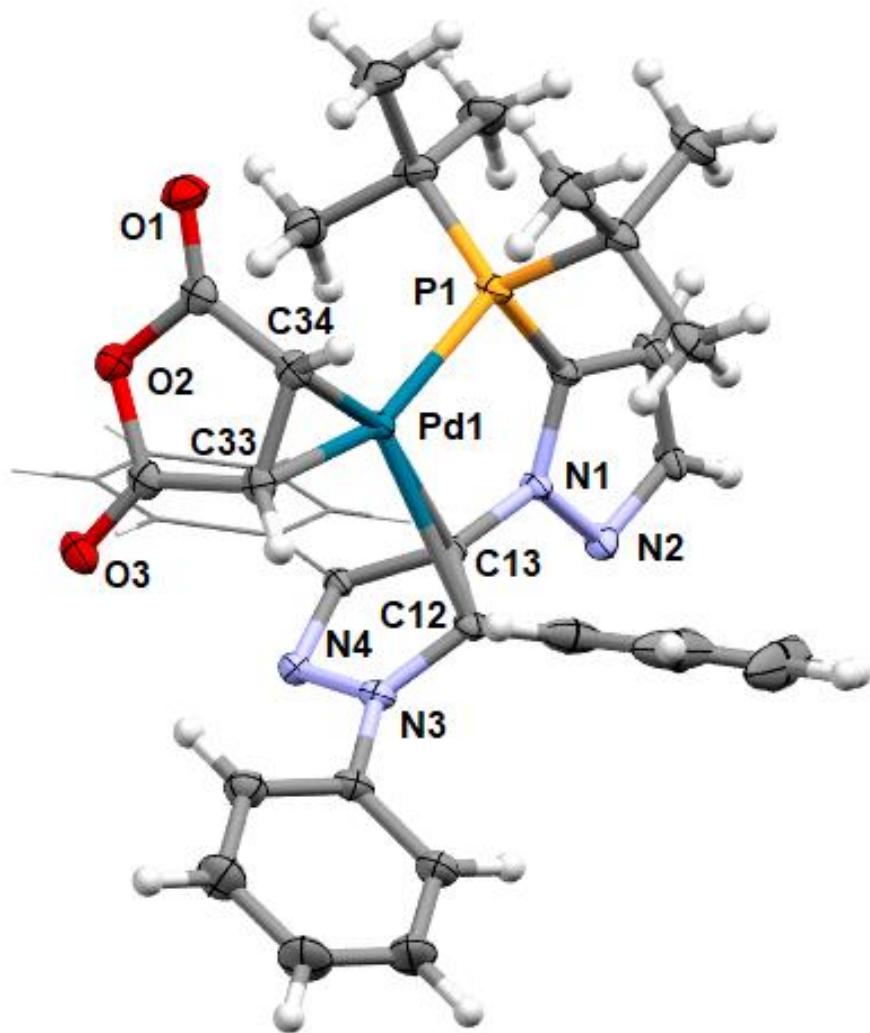


Figure S73. Solid-state molecular structure of complex **12**, excluding disordered diethyl ether and dichloromethane solvates. Thermal ellipsoids plotted at 50% probability for non-H atoms; H-atoms shown as uniformly-sized white spheres for clarity. One phenyl group is shown in wireframe for clarity. Selected bond lengths (\AA) and angles ($^\circ$): Pd1–P1: 2.3051(8); Pd1–C13: 2.367(3); Pd1–C12: 2.622(3); Pd1–C33: 2.133(3); Pd1–C34: 2.081(3); C33–C34: 1.422(4); P1–Pd1–C13: 84.55(6); P1–Pd1–C34: 114.71(8); C13–Pd1–C33: 121.37(10).

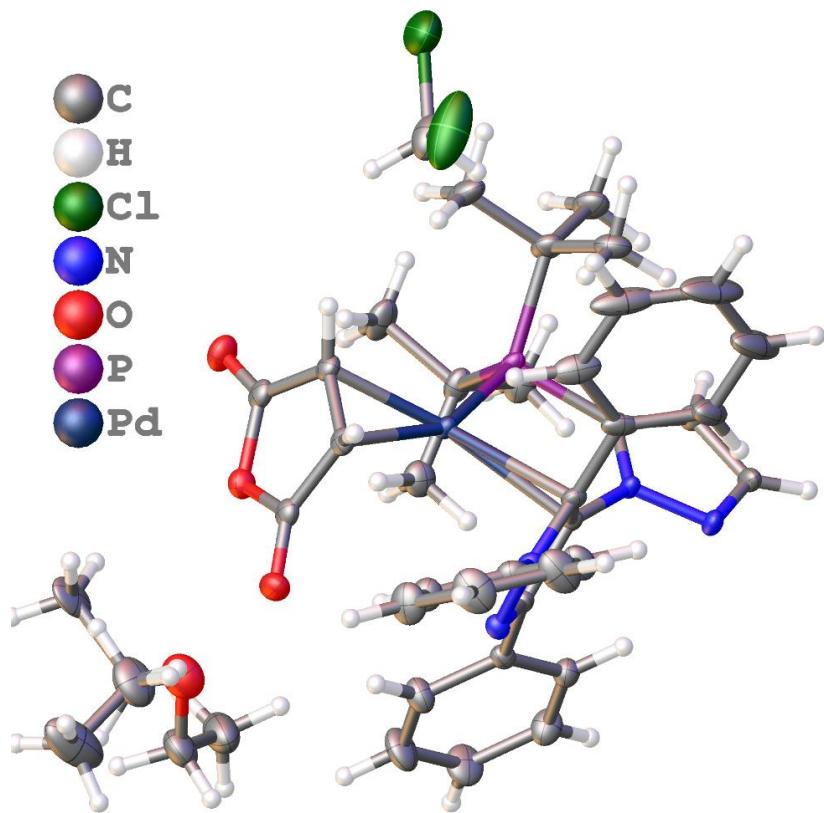
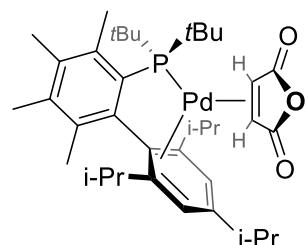


Figure S74. Solid-state molecular structure of complex **12**, including disordered half-occupancy diethyl ether and full-occupancy dichloromethane solvates. Thermal ellipsoids plotted at 50% probability for non-H atoms; H-atoms shown as uniformly-sized white spheres for clarity.

Me₄tBuXPhos–Pd–MAH (13)

Prepared according to the general procedure using **1** (101.8 mg, 0.2171 mmol), Me₄tBuXPhos (109.6 mg, 0.2126 mmol), and THF (11 mL). Trituration/decantation 7 x with hexanes (5 mL). Yellow solid: 75.7 mg (51%). ¹H NMR: (300 MHz, C₆D₆) δ 0.53 (d, 9H, *J* = 15.0 Hz), 0.77 (d, 9H, *J* = 15.3 Hz), 1.41 (m, 4H, THF), 3.57 (m, 4H, THF), 3.89 (dd, 1H, *J* = 4.2, 5.9 Hz) 4.11 (d, 1H, *J* = 4.1 Hz), 6.07 (d, 1H, *J* = 2.0 Hz), 6.80-7.02 (m, 8H), 7.06 (m, 2H), 7.41 (m, 2H), 7.76-7.86 (m, 5H); ¹³C{¹H} NMR: (125 MHz, CD₂Cl₂) δ 28.7 (d, *J* = 8.3 Hz), 28.8 (d, *J* = 8.3 Hz), 34.5 (d, *J* = 13.6 Hz), 34.7 (d, *J* = 13.3 Hz), 51.3 (d, *J* = 14.2 Hz), 54.8 (d, *J* = 2.2 Hz), 107.7, 113.3, 125.9, 127.7, 127.8, 128.2, 128.6, 128.8, 128.9, 129.3, 139.0, 130.3, 130.8, 139.3, 140.8, 144.1 (d, *J* = 29.3 Hz), 144.4 (d, *J* = 5.8 Hz), 150.7, 169.2 (d, *J* = 3.3 Hz), 170.4; ³¹P{¹H} NMR: (121 MHz, C₆D₆) δ 46.6. Yield: 43%; ¹H NMR: (500 MHz, CD₂Cl₂) δ 0.83 (d, 3H, *J* = 6.0 Hz), 0.88 (d, 3H, *J* = 6.0 Hz), 1.13 (s, 3H), 1.24 (d, 3H, *J* = 5.8 Hz), 1.35 (d, 3H, *J* = 5.6 Hz), 1.38-1.60 (m, 24H), 2.01 (m, 1H), 2.21 (s, 3H), 2.21 (s, 3H), 2.40 (br m, 2H), 2.63 (s, 3H), 3.15 (sept, 1H, *J* = 6.9 Hz), 4.24 (br s, 1H), 7.25 (s, 1H), 7.40 (s, 1H); ¹³C{¹H} NMR: (500 MHz, CD₂Cl₂) δ 17.0, 17.1, 19.6, 23.1, 24.2, 24.4, 25.6, 26.3, 26.5, 31.4 (d, *J* = 30.2 Hz), 32.5, 32.6, 32.7, 32.7, 33.9, 38.7 (d, *J* = 3.6 Hz), 58.0 (d, *J* = 29.7 Hz), 58.6, 117.9 (d, *J* = 4.5 Hz), 122.4, 124.5, 125.9, 126.3, 128.1, 135.5 (d, *J* = 10.3 Hz), 136.4 (d, *J* = 12.4 Hz), 136.6 (d, *J* = 4.3 Hz), 138.8, 139.3, 139.6 (d, *J* = 1.5 Hz), 145.6 (d, *J* = 35.2 Hz), 147.2, 149.3, 163.5, 169.8; ³¹P{¹H} NMR: (300 MHz, C₆D₆) δ 89.6. HRMS (ESI) of [C₃₇H₅₅O₃PPd•H] (major isotopomer, H⁺ adduct): 685.29964 (calc'd); 685.29954 (found). Elemental analysis (CH) of C₃₇H₅₅O₃PPd: 64.85, 8.09 (calc'd); 64.08, 8.05 (actual).



Me₄tBuXPhos-Pd-MAH (13)
51% isolated

The formation of **13** from either complex **1** or the *tert*-butyl analogue and two equivalents of Me₄tBuXPhos at room temperature was followed by ¹H and ³¹P NMR spectroscopy using the following procedure. Inside a nitrogen glovebox, a 1.8 mL HPLC vial was charged with Me₄tBuXPhos (13.0 mg, 0.0271 mmol) and CDCl₃ (0.2 mL). The vial was sealed with an aluminum crimp cap containing a PTFE-lined rubber septum and removed from the glovebox. An NMR tube was charged with either ^{DMP}DAB–Pd–MAH (**1**, 6.3 mg, 0.0134 mmol) or ^{tBu}DAB–Pd–MAH (5.0 mg, 0.0134 mmol) and 1,3,5-trimethoxybenzene (0.00402 mmol, added as a stock solution in CDCl₃) with a total CDCl₃ volume of 0.5 mL, and the tube capped with a small rubber septum. An initial ¹H NMR spectrum was obtained to lock and shim on the sample, and to establish the relative integration between the signals for the starting Pd complexes and the internal standard. The solution of Me₄tBuXPhos was then added to the NMR tube via syringe, and both ¹H and ³¹P NMR spectra were taken at regular intervals to monitor the reaction progress (Figure S75).

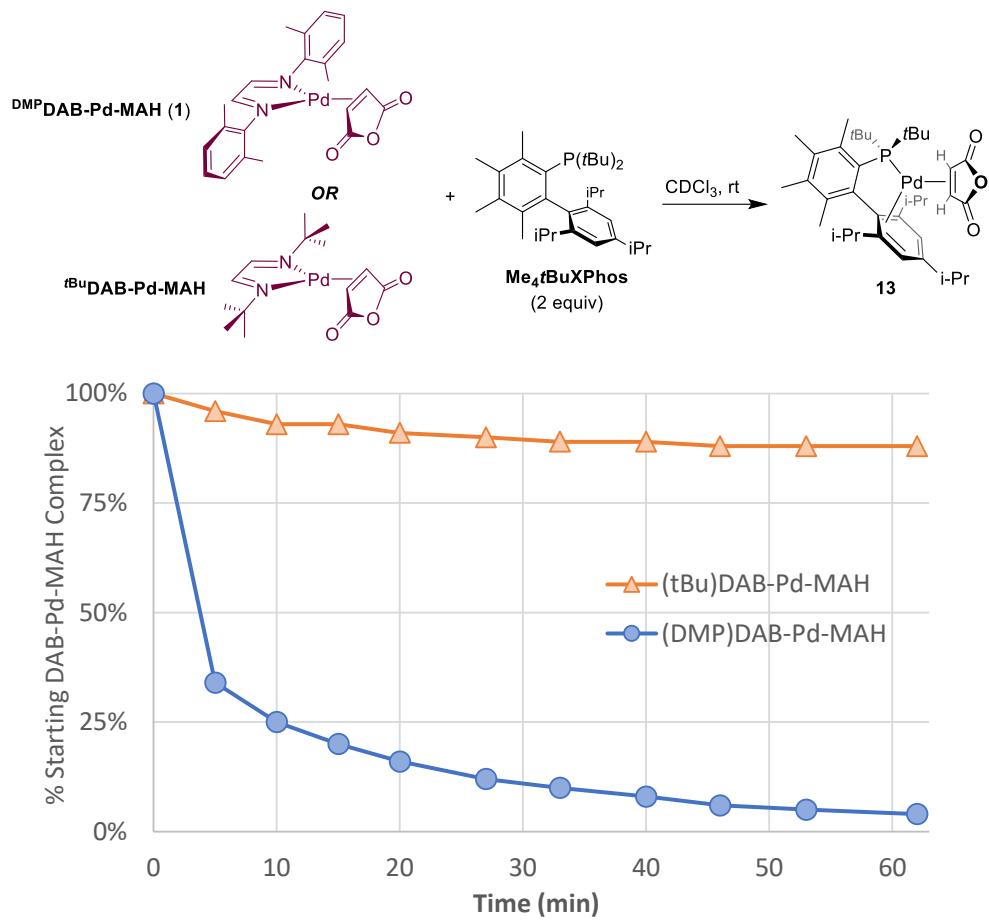


Figure S75. Comparison of ligand substitution reaction progress between ^{DMP}DAB–Pd–MAH (**1**) or ^{tBu}DAB–Pd–MAH and Me₄tBuXPhos (2 equiv) to generate **13**. Complex **1** is >95% converted after 60 min, whereas ~90% of ^{tBu}DAB–Pd–MAH remains after the same time period.

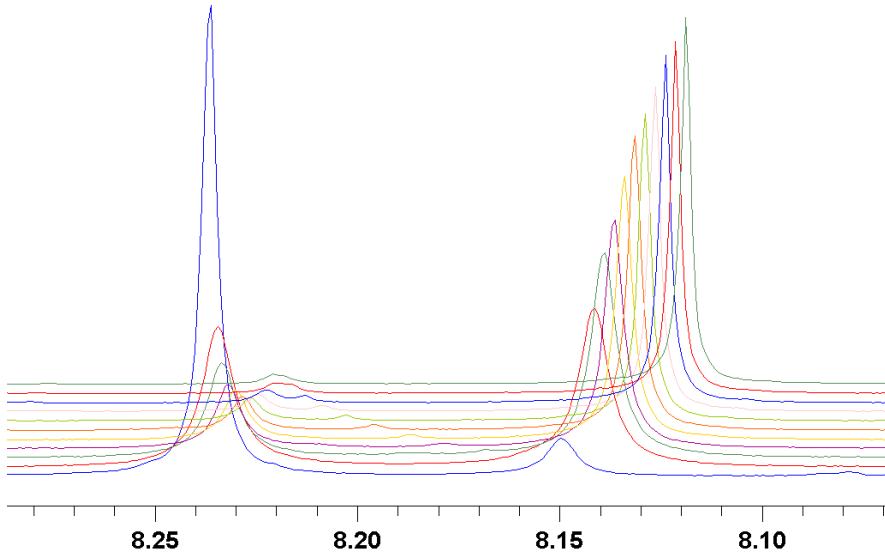


Figure S76. ^1H NMR spectrum stack plot of the ligand substitution between $^{\text{DMP}}\text{DAB-Pd-MAH}$ (**1**) (singlet at 8.24 ppm) and $\text{Me}_4\text{tBuXPhos}$ (2 equiv), with time increasing from front (0 min) to back (62 min).
Singlet at 8.15 ppm is free $^{\text{DMP}}\text{DAB}$ (displaced by $\text{Me}_4\text{tBuXPhos}$).

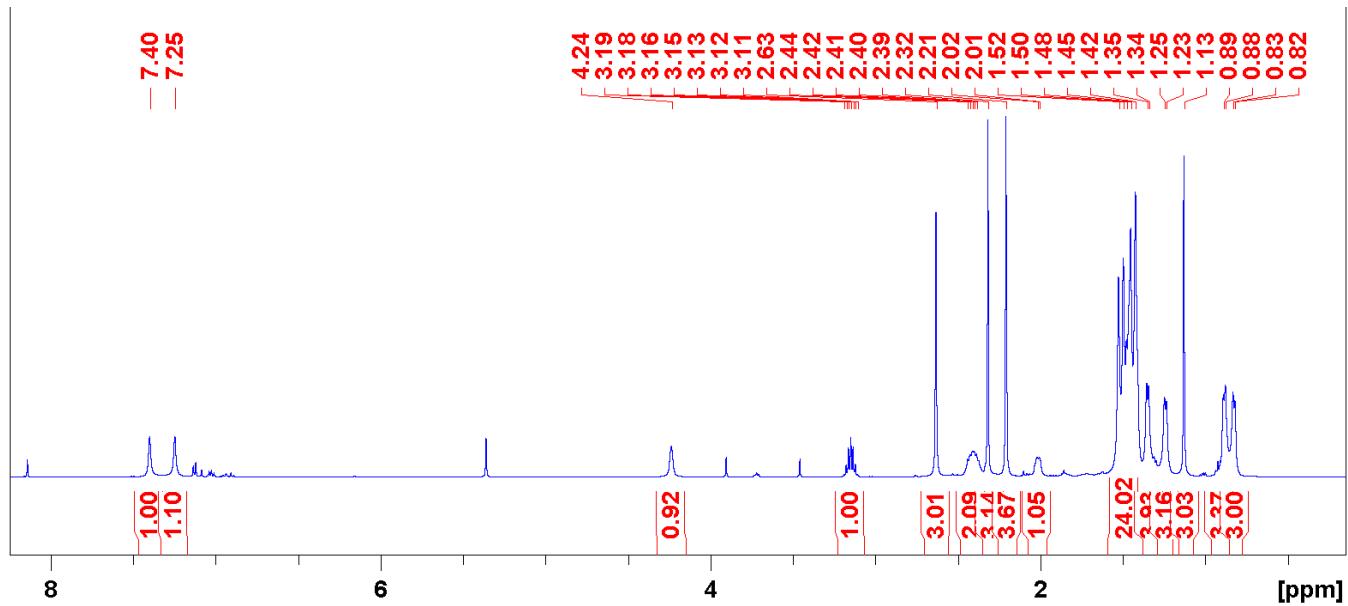


Figure S77. ^1H NMR spectrum (500 MHz; CD_2Cl_2) of **13**.

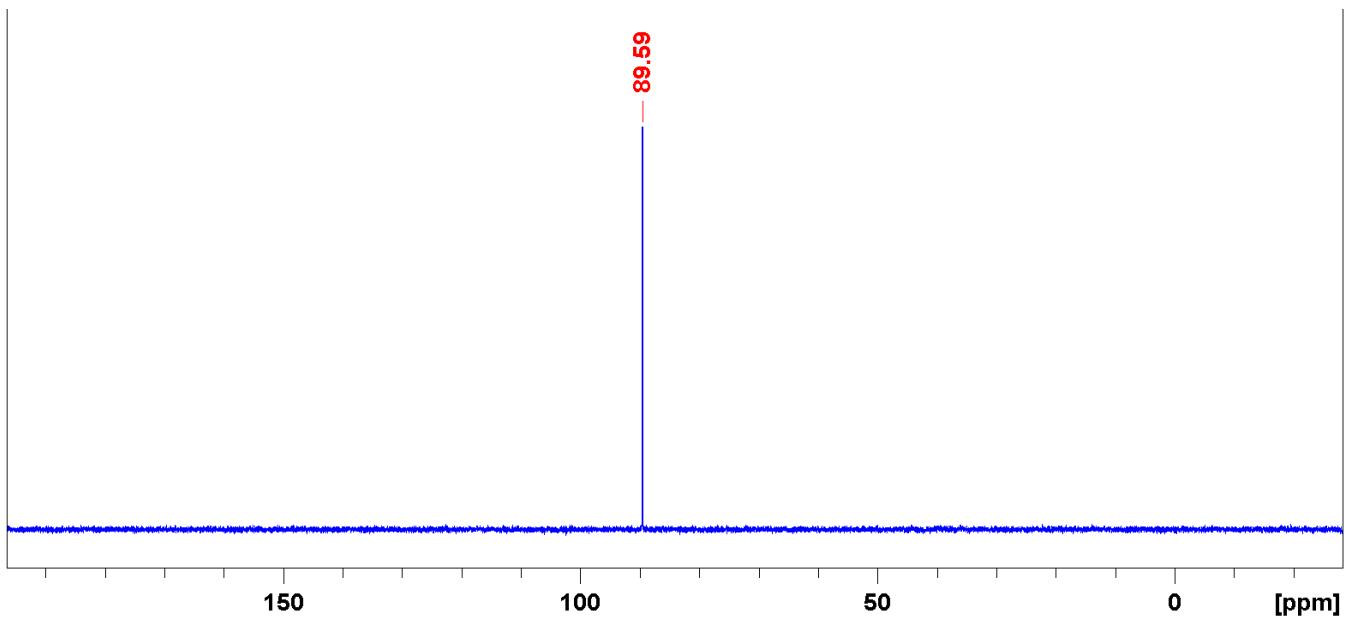


Figure S78. ^{31}P NMR spectrum (300 MHz, C_6D_6) of **13**.

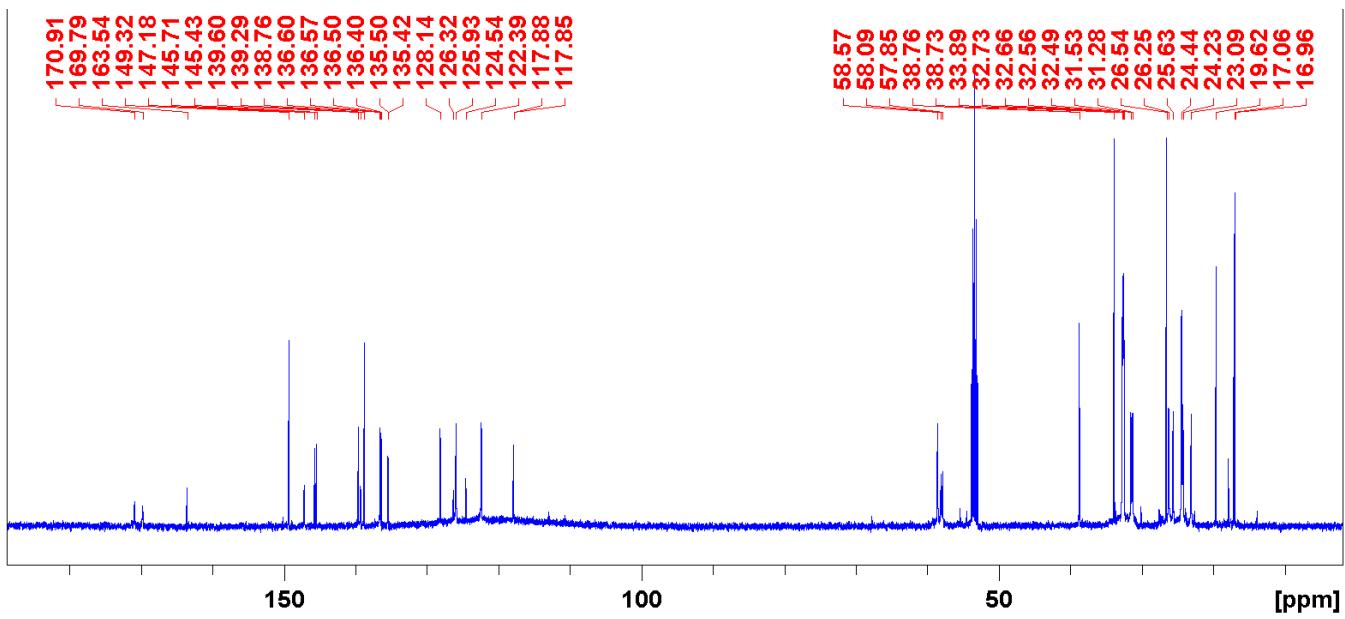


Figure S79. ^{13}C NMR spectrum (125 MHz; CD_2Cl_2) of **13**.

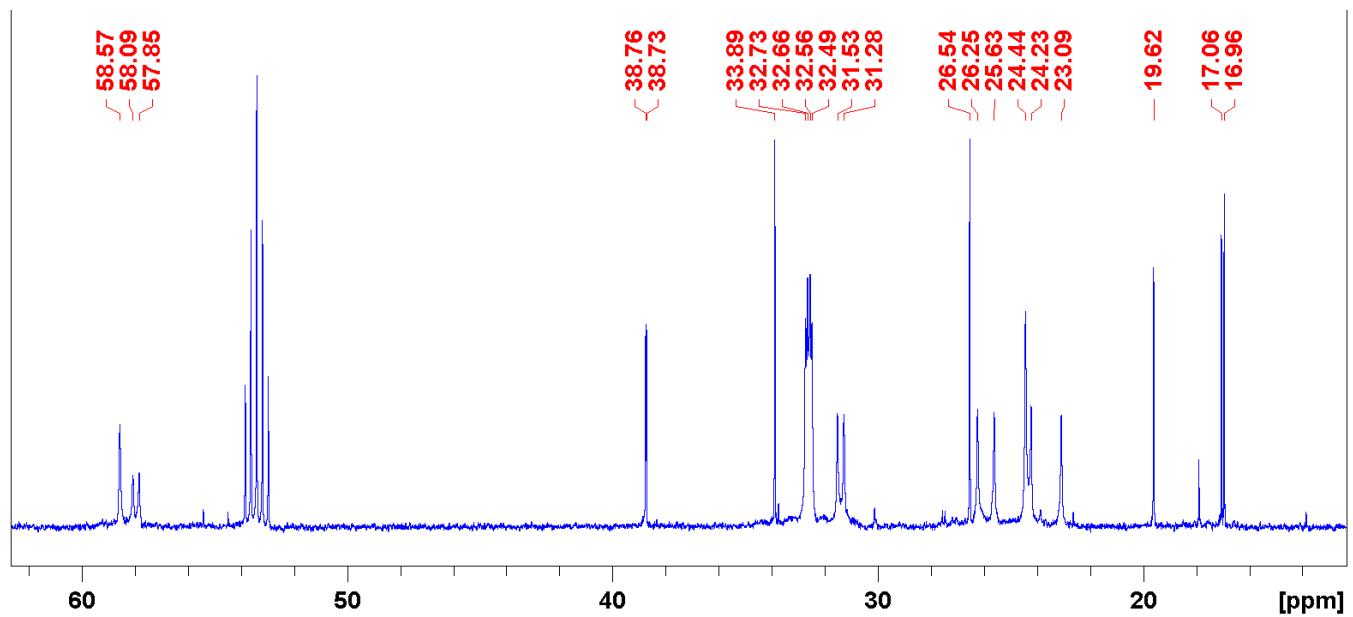


Figure S80. ^{13}C NMR spectrum (125 MHz; CD_2Cl_2) of **13**. Expansion of aliphatic region.

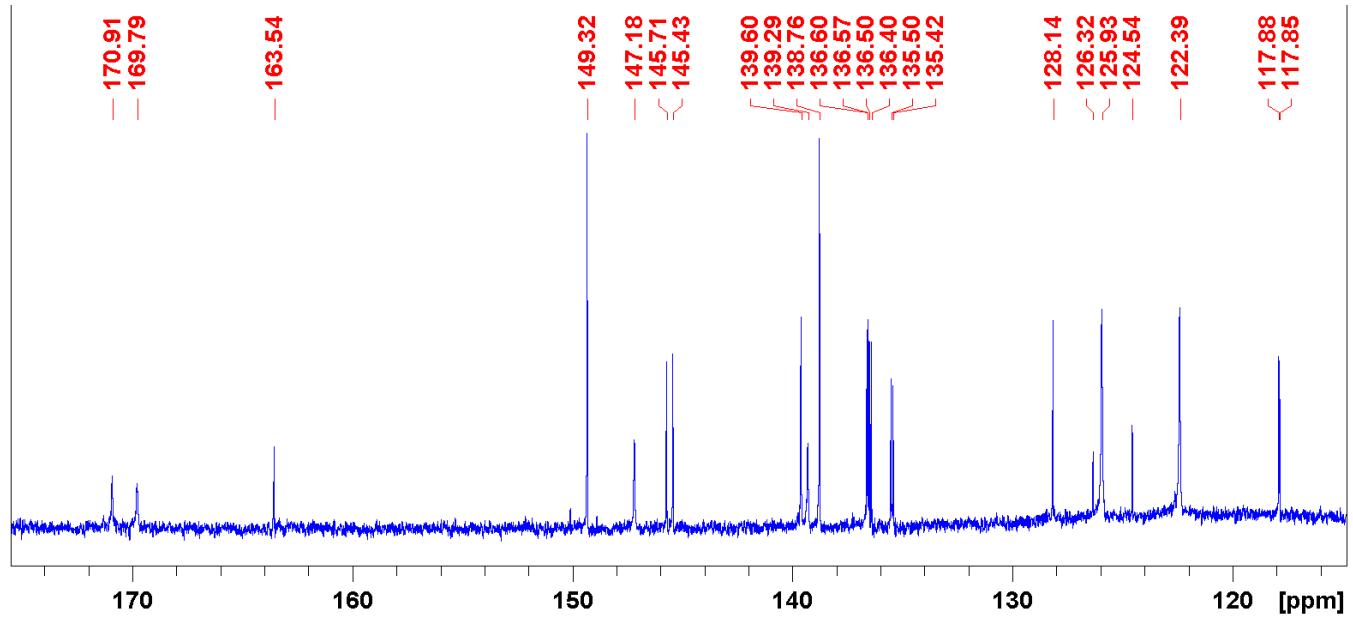


Figure S81. ^{13}C NMR spectrum (125 MHz; CD_2Cl_2) of **13**. Expansion of aromatic region.

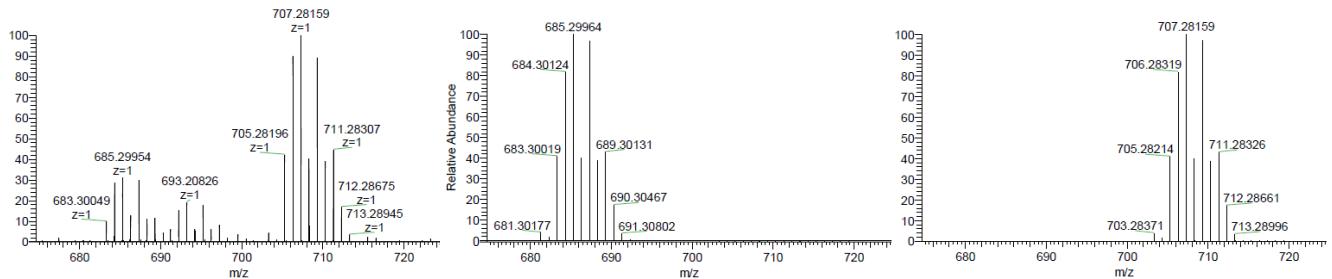
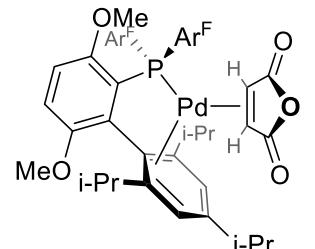


Figure S82. *Left:* Experimental HRMS-ESI spectrum of $[\mathbf{13} \bullet \text{H}]^+$ and $[\mathbf{13} \bullet \text{Na}]^+$. *Middle:* Calculated HRMS isotope pattern for $[\mathbf{13} \bullet \text{H}]^+$. *Right:* Calculated HRMS isotope pattern for $[\mathbf{13} \bullet \text{Na}]^+$.

JackiePhos-Pd-MAH (14)

Prepared according to the general procedure using **1** (56.5 mg, 0.1205 mmol), JackiePhos (100.8 mg, 0.1265 mmol), and THF (4 mL). Trituration/decantation 6 x with hexanes (4 mL). Yellow solid: 66.4 mg (55%). ^1H NMR: (500 MHz, CD_2Cl_2) δ 0.93 (br s, 3H), 0.97 (br s, 3H), 1.08 (br s, 3H), 1.29 (br s, 3H), 1.43 (br s, 3H), 1.46 (br s, 3H), 2.19 (Br s, 3H), 2.33 (br s, 1H), 2.26 (br d, 1H, J = 6.9 Hz), 3.15 (sept, 1H, J = 6.9 Hz), 3.57 (s, 3H), 3.62 (s, 3H), 4.32 (br s, 1H), 7.06 (dd, 1H, J = 2.8 Hz, 9.0 Hz), 7.17 (d, 1H, J = 8.9 Hz), 7.44 (br s, 1H), 7.46 (br s, 1H), 7.77-7.90 (m, 2H), 7.95-8.13 (m, 4H); $^{13}\text{C}\{\text{H}\}$ NMR: (125 MHz, CD_2Cl_2) δ 22.8, 23.6, 24.3, 24.6, 25.2, 32.1, 33.9, 54.9, 55.1, 59.3 (d, J = 29.3 Hz), 60.1, 112.3 (d, J = 5.5 Hz), 116.5 (d, J = 7.0 Hz), 116.6, 119.8, 120.6, 122, 122.4 (d, J = 38.2 Hz), 122.9, 124.1, 124.2, 125.0, 126.3, 131.5 q (J = 33.4 Hz), 131.6 q (J = 33.5 Hz), 132.6, 133.5, 136.0 (d, J = 34.9 Hz), 137.7 (d, J = 38.0 Hz), 141.4, 144.3, 149.5, 152.7 (d, J = 18.8 Hz), 154.7 (d, J = 3.0 Hz), 168.5, 168.7; $^{31}\text{P}\{\text{H}\}$ NMR: (202 MHz, CD_2Cl_2) δ 28.9; $^{19}\text{F}\{\text{H}\}$ NMR: (282 MHz, CD_2Cl_2) δ 63.4. HRMS (ESI) of $[\text{C}_{43}\text{H}_{39}\text{F}_{12}\text{O}_5\text{PPd} \bullet \text{H}]^+$ (major isotopomer, H^+ adduct): 1001.14511 (calc'd); 1001.14681 (found). Elemental analysis (CH) of $\text{C}_{43}\text{H}_{39}\text{F}_{12}\text{O}_5\text{PPd}$: 51.59, 3.93 (calc'd); 51.84, 4.08 (actual).



JackiePhos-Pd-MAH (14)

(Ar^F = 3,5-(CF_3)-Ph)

55% isolated

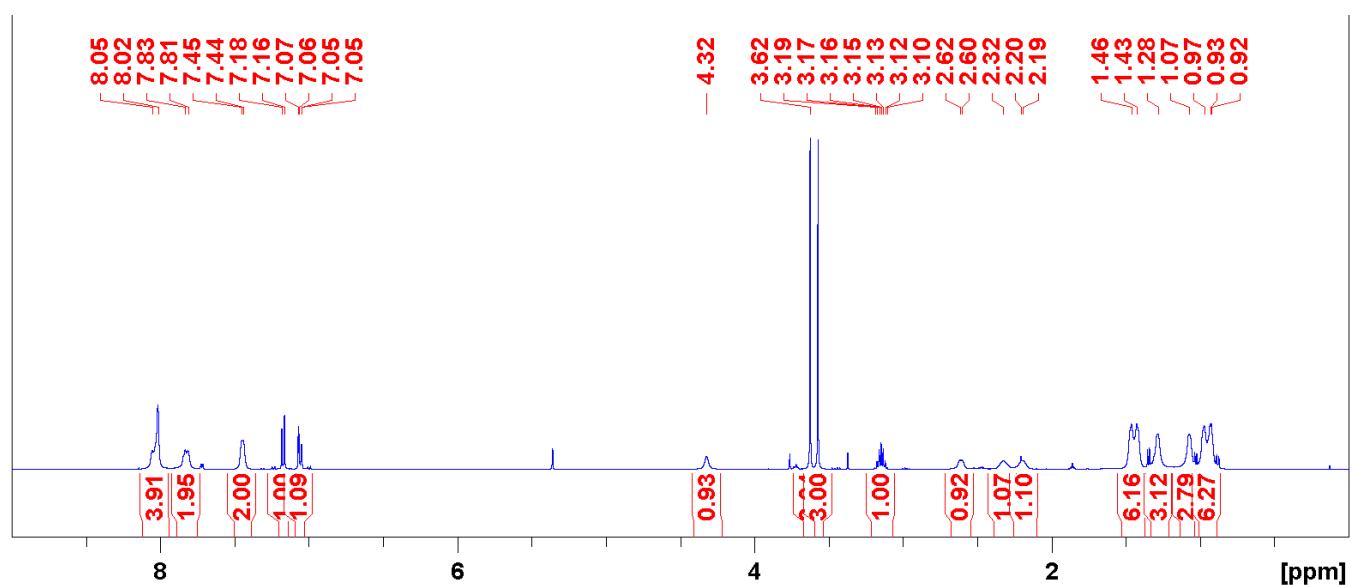


Figure S83. ^1H NMR spectrum (500 MHz; CD_2Cl_2) of **14**.

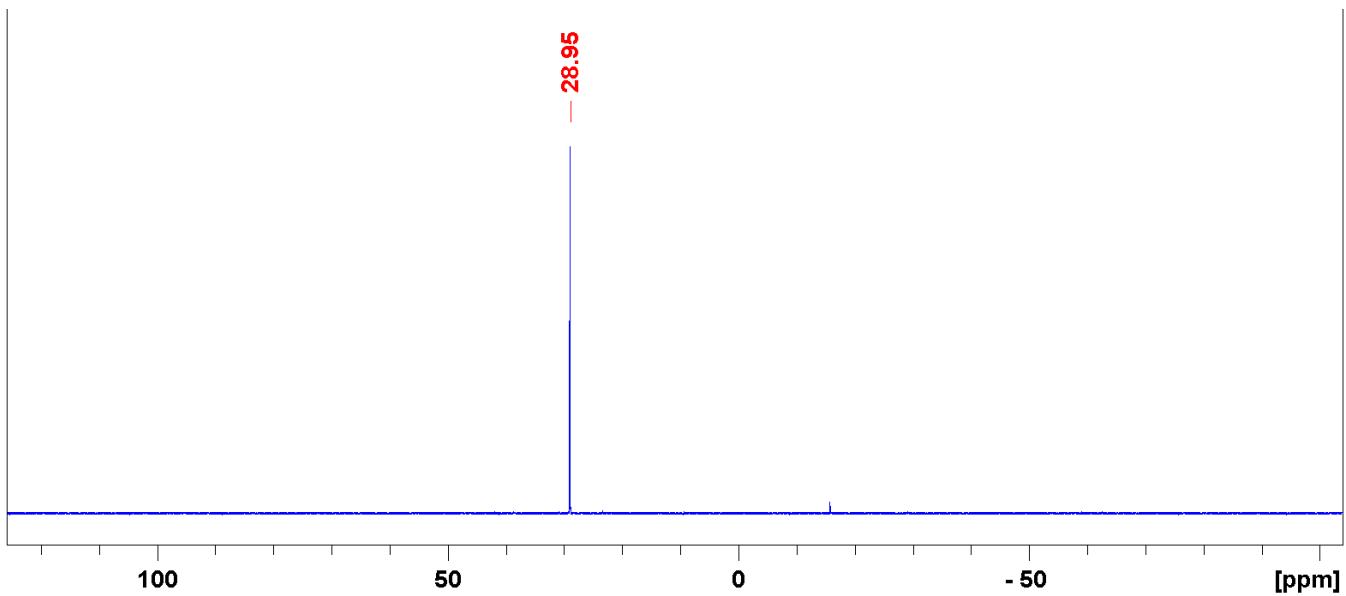


Figure S84. ^{31}P NMR spectrum (202 MHz; CD_2Cl_2) of **14**.

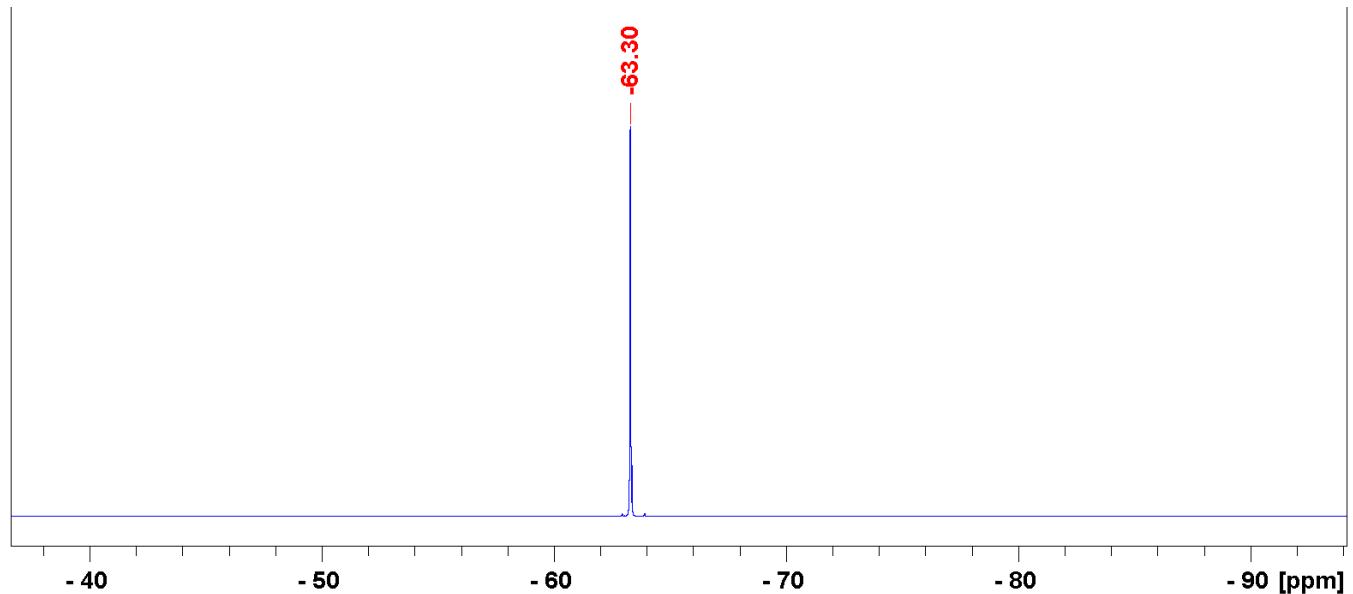


Figure S85. ^{19}F NMR spectrum (282 MHz; CD_2Cl_2) of **14**.

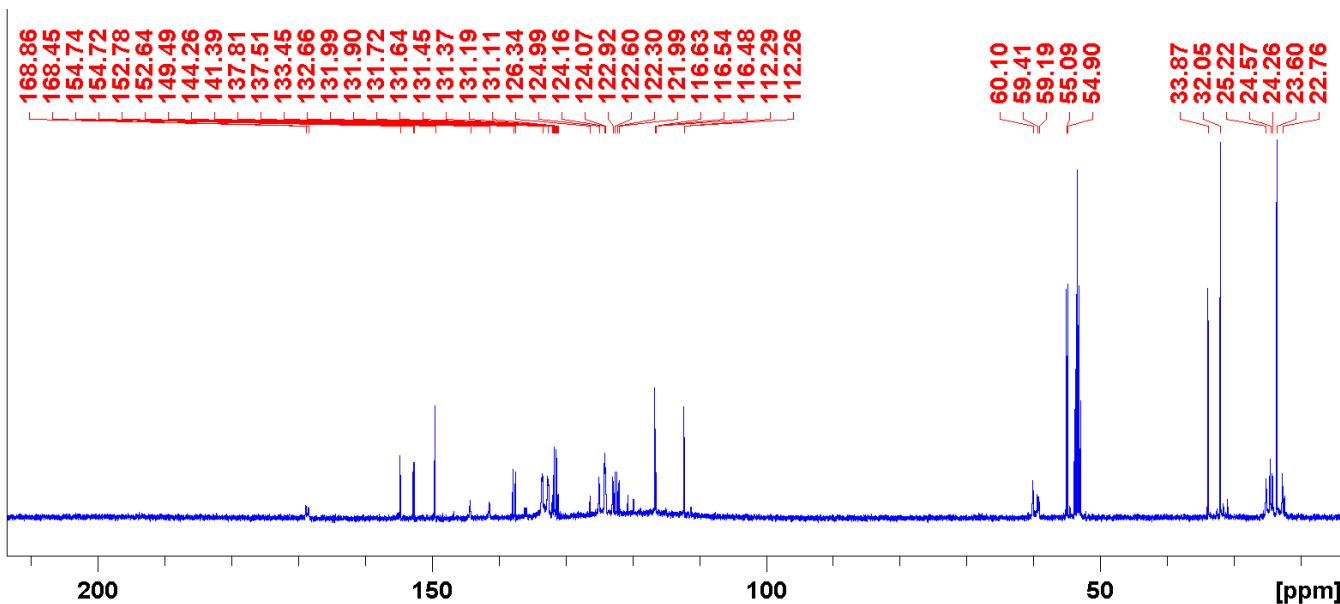


Figure S86. ¹³C NMR spectrum (125 MHz; CD₂Cl₂) of **14**.

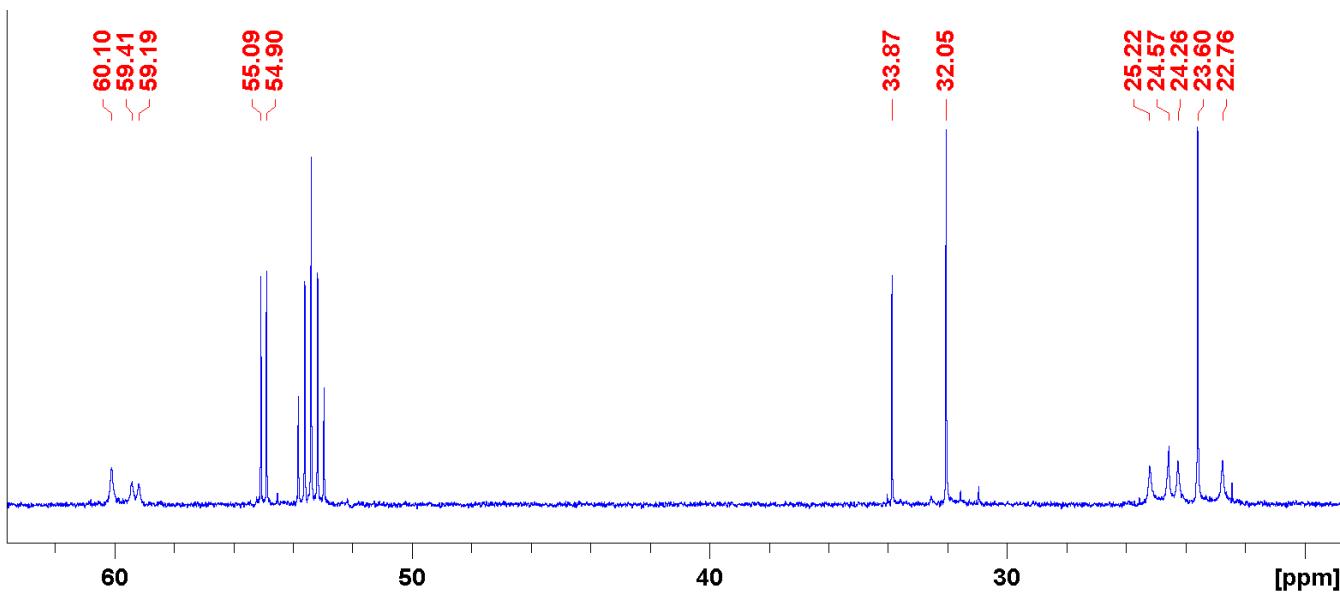


Figure S87. ¹³C NMR spectrum (125 MHz; CD₂Cl₂) of **14**. Expansion of aliphatic region.

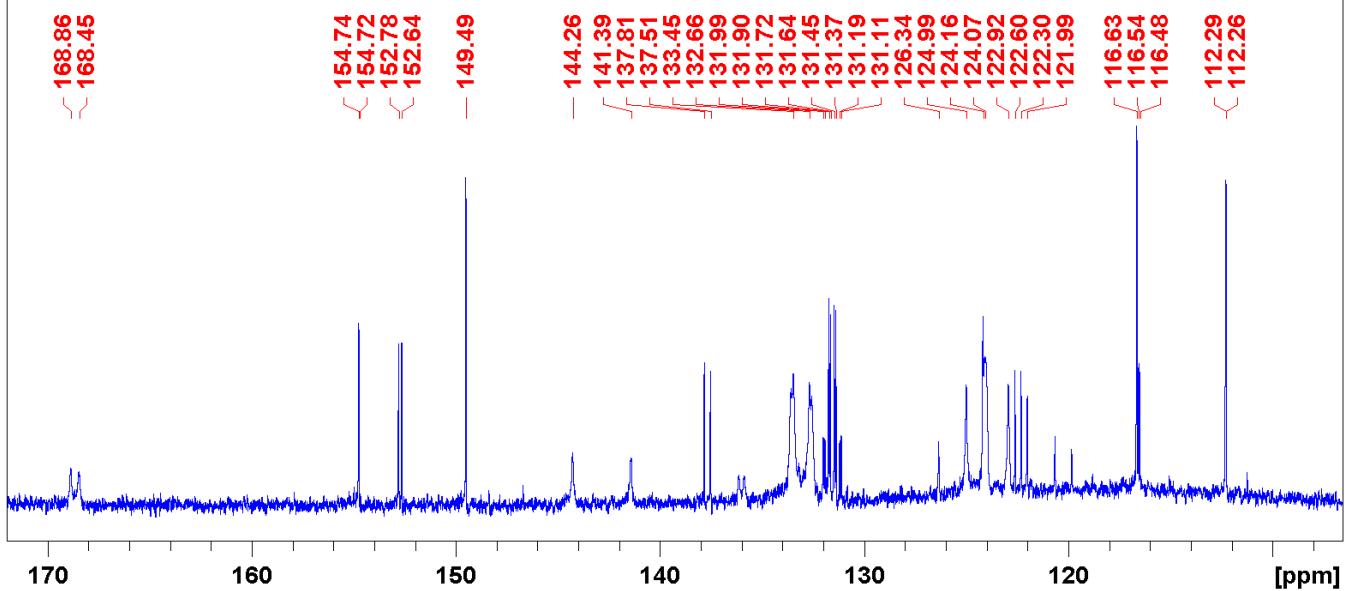


Figure S88. ^{13}C NMR spectrum (125 MHz; CD_2Cl_2) of **14**. Expansion of aromatic region.

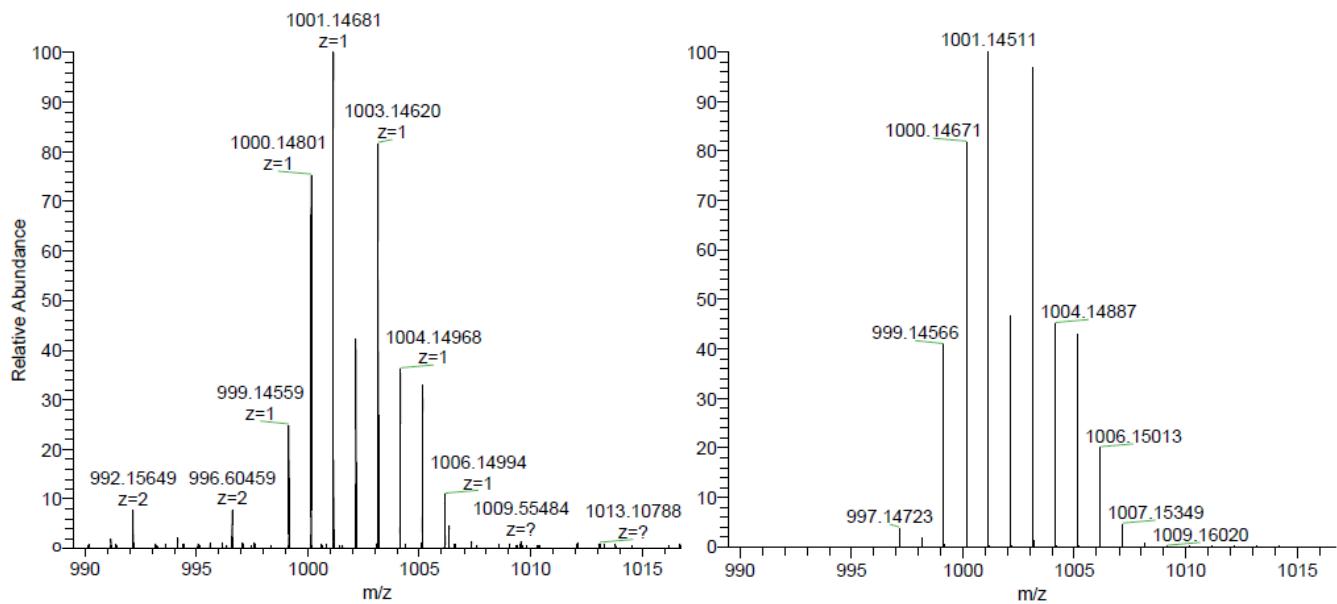


Figure S89. *Left:* Experimental HRMS-ESI spectrum of $[\mathbf{14}\bullet\text{H}]^+$. *Right:* Calculated HRMS isotope pattern for $[\mathbf{14}\bullet\text{H}]^+$.

The ligand substitution progress for four phosphines and one NHC reacting with complex **1** at room temperature was followed by ^1H NMR spectroscopy using the following procedure. Inside a nitrogen glovebox, a 1.8 mL HPLC vial was charged with ligand (0.0134 mmol for DPEPhos and DIPP-NHC; 0.0271 mmol for monodentate phosphines) and d_8 -THF (0.2 mL). The vial was sealed with an aluminum crimp cap containing a PTFE-lined rubber septum and removed from the glovebox. An NMR tube was charged with $^{DMP}\text{DAB-Pd-MAH}$ (**1**, 6.3 mg, 0.0134 mmol) and 1,3,5-trimethoxybenzene (\sim 0.0134 mmol) with a total d_8 -THF volume of 0.5 mL, and the tube capped with a screw-cap containing a septum. An initial ^1H NMR spectrum was obtained to lock and shim on the sample, and to establish the relative integration between the signals for the starting Pd complex and the internal standard. The solution of phosphine was then added to the NMR tube via syringe, and ^1H NMR spectra were taken at regular intervals to monitor the reaction progress (Figure S90).

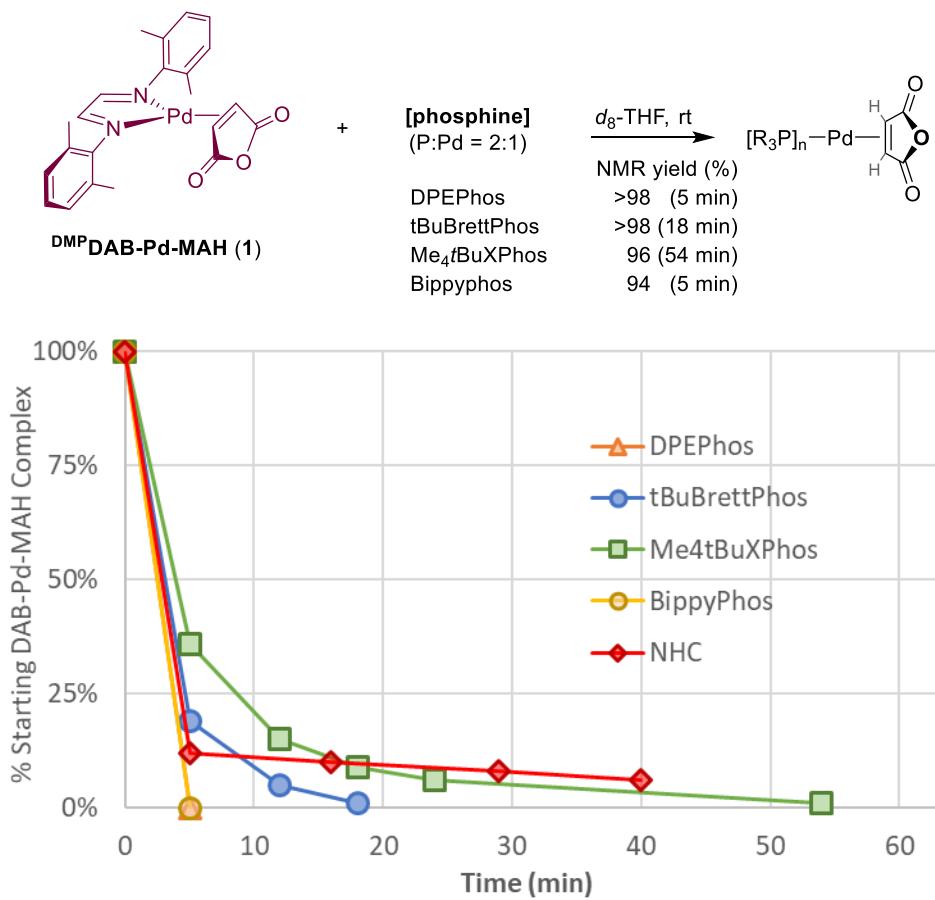


Figure S90. Comparison of ligand substitution reaction progress between $^{DMP}\text{DAB-Pd-MAH}$ (**1**) and several phosphines (P:Pd = 2) or *N,N'*-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (DIPP-NHC, 1 equiv per Pd) to generate [ligand]-Pd-MAH complexes. Both DPEPhos and BippyPhos result in >95% substitution in less than 5 minutes. NMR yields determined by relative integration of product signals to 1,3,5-trimethoxybenzene internal standard. For DIPP-NHC, while immediate ligand substitution is apparent (\sim 90% conversion of **1** in 5 min), the ^1H NMR spectra indicate the presence of multiple species (Figure S91).

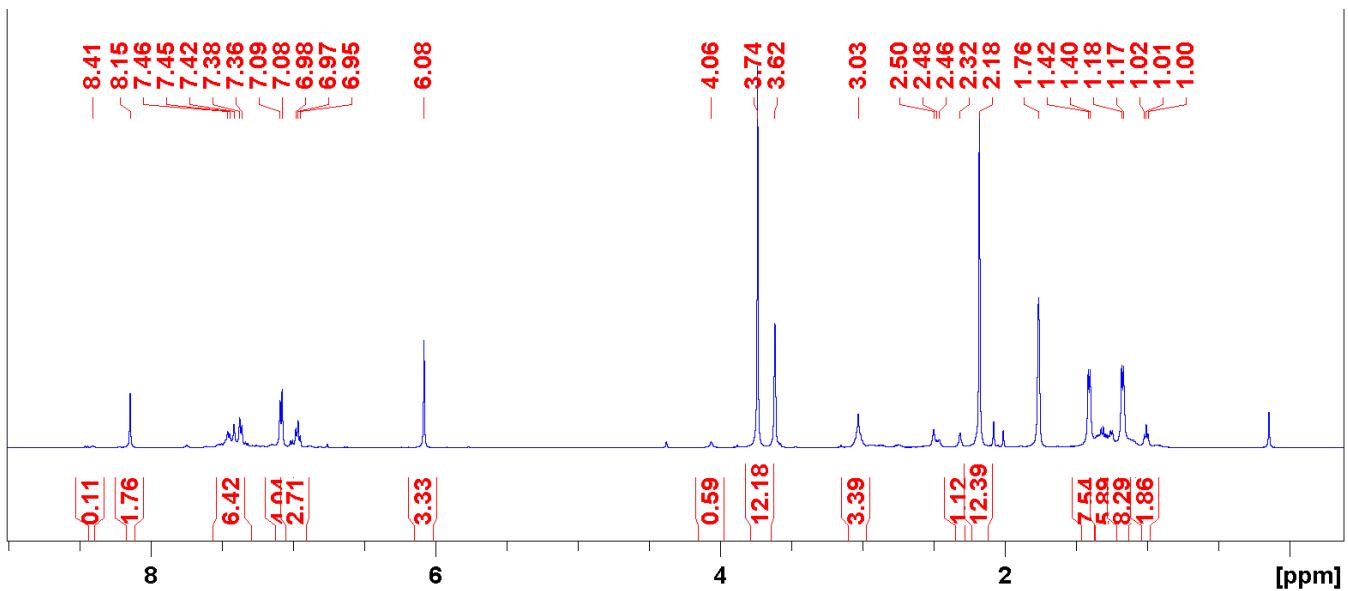


Figure S91. ¹H NMR spectrum of the reaction between **1** and DIPP-NHC (1 equiv).

III: High-Throughput Screening

General Procedure for High-Throughput Screening

The coupling of 2-chloropyridine and benzylamine (1° amine screen from Figure 6) is given here as an example.

Preparation of palladium sources:

Four different palladium precatalysts were dissolved in corresponding solvents with high solubility in four different vials. 21.0 mg (0.0936 mmol) of palladium acetate was dissolved in 1348 μL of dichloromethane. 17.1 mg (0.0468 mmol) of allylpalladium(II) chloride dimer was dissolved in 2269 μL of acetone. 48.4 mg (0.0468 mmol) of recrystallized $\text{Pd}_2\text{dba}_3 \bullet \text{CHCl}_3$ was dissolved in 1968 μL of tetrahydrofuran. 43.9 mg of DAB-Pd-MAH (0.0936 mmol) was dissolved in 2235 μL of acetone. These palladium sources stock solutions were dispensed into a 96-well-plate (24 wells for each palladium source). 40 μL of palladium acetate stock solution was dispensed into each of the 24 wells. 63.3 μL of allylpalladium chloride dimer stock solution was dispensed into each of the 24 wells. 56.3 μL of $\text{Pd}_2\text{dba}_3 \bullet \text{CHCl}_3$ stock solution was dispensed into each of the 24 wells. 63.3 μL of ^{DMP}DAB-Pd-MAH stock solution was dispensed into each of the 24 wells. The solvents were then evaporated through using Genevac. The 96-well-plate was stored in the glovebox for the further use.

Preparation of phosphine ligands:

The ratio between the Pd loading and phosphine ligands is 2:1. Inside the glovebox, 0.0624 mmol of each phosphine ligand (33.5 mg of BrettPhos, 29.7 mg of XPhos, 26.5 mg of *t*BuXPhos, 30.2 mg *t*BuBrettPhos, 29.1 mg of RuPhos, 29.2 μL of $\text{P}(\text{tBu})_3$) was dissolved in 600 μL of THF in 4-dram vials separately. 100 μL of each ligand stock solution was weighed, and the mass was recorded. 0.0052 mmol of each ligand stock solution (51.5 μL of BrettPhos stock solution, 53.3 μL of XPhos stock solution, 51.9 μL of *t*BuXPhos stock solution, 51.7 μL of *t*BuBrettPhos stock solution, 51.5 μL of RuPhos stock solution and 52.4 μL of $\text{P}(\text{tBu})_3$) was dispensed into each of four wells containing four different palladium sources.

Preparation of reaction stock solution:

A vial was in charge with 67.9 μL (0.72 mmol) of 2-chloropyridine, 78.8 μL (0.72 mmol) of benzylamine, 207.6 (2.16 mmol) mg of NaO-tBu , 36.3 mg (0.216 mmol) of 1,3,5-trimethoxybenzene, 5.4 mL of THF and a stir bar. After being mixed well, 161.1 μL of this reaction stock solution was added into each well. The top of 24-well-plate was screwed on, and the whole plate was taken out form the glovebox. The plate was placed on the hot plate and stirred for 3 hours at 80 °C.

Analysis of 24-well reactions:

500 μL of acetonitrile was added to each well once the reaction was stopped for diluting the reaction mixtures. 40 μL of each diluted reaction mixture was then transferred to 24 different HPLC vials followed by the addition of 1 mL of acetonitrile. These 24 samples were analyzed by the HPLC/UV-VIS detector.

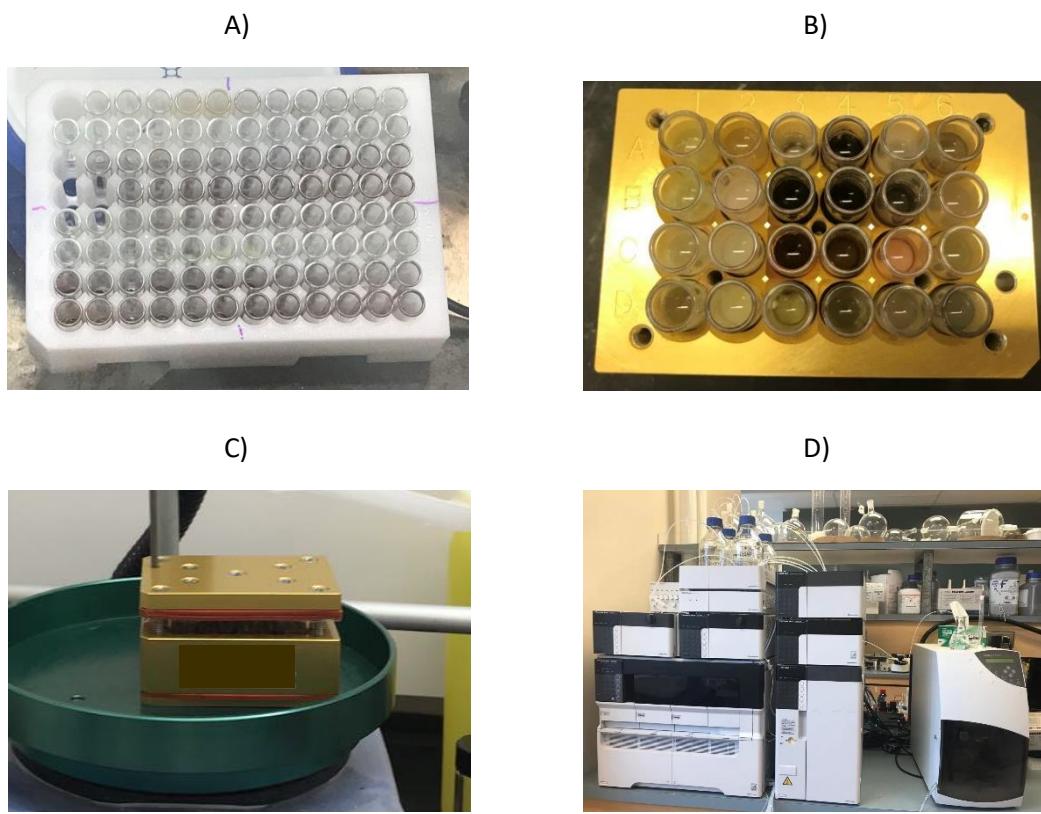


Figure S92. General procedure for running microscale high-throughput screens. A) Well-prepared palladium sources. B) Addition of reaction stock solutions and phosphine ligands. C) 24-well plate for running the reaction. D) Analysis by HPLC/UV-VIS.

High-Throughput Screening Data

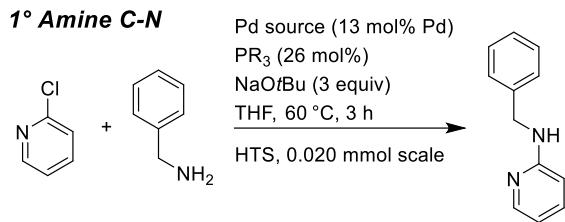


Table S2. UPLC gradient profile in primary amine C-N coupling.

Time (min)	Mobile Phase B (ACN) %	Flow Rate (mL/min)	Injection Volume (μL)
0.01	15	0.8	5
0.01-3.5	15-85		
3.5-3.6	85-15		
3.6-4.5	15		

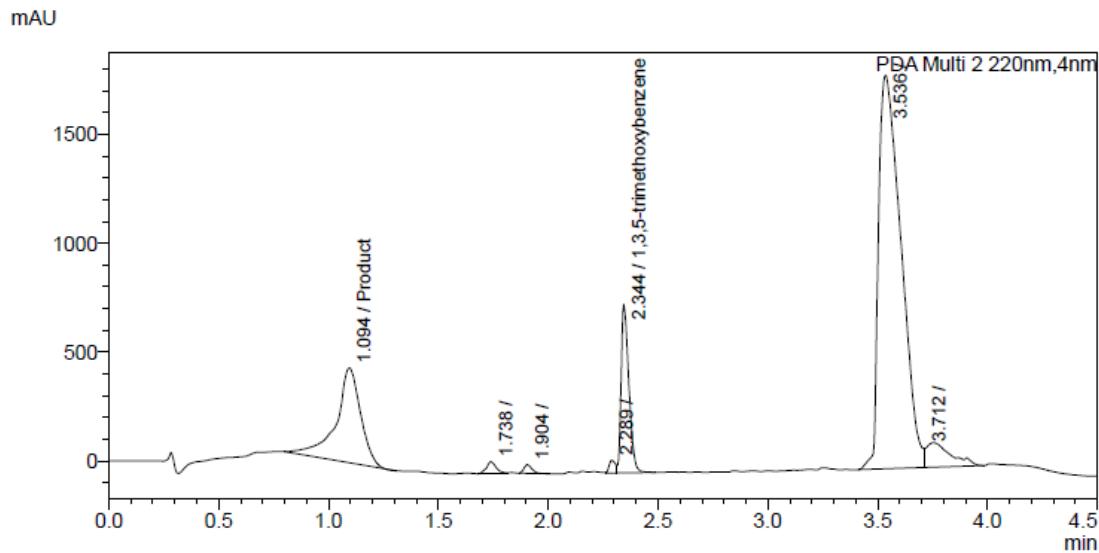


Figure S93. Representative UPLC trace for primary C-N coupling ($^{\text{DMP}}$ DAB-Pd-MAH/tBuBrettPhos)

mAU

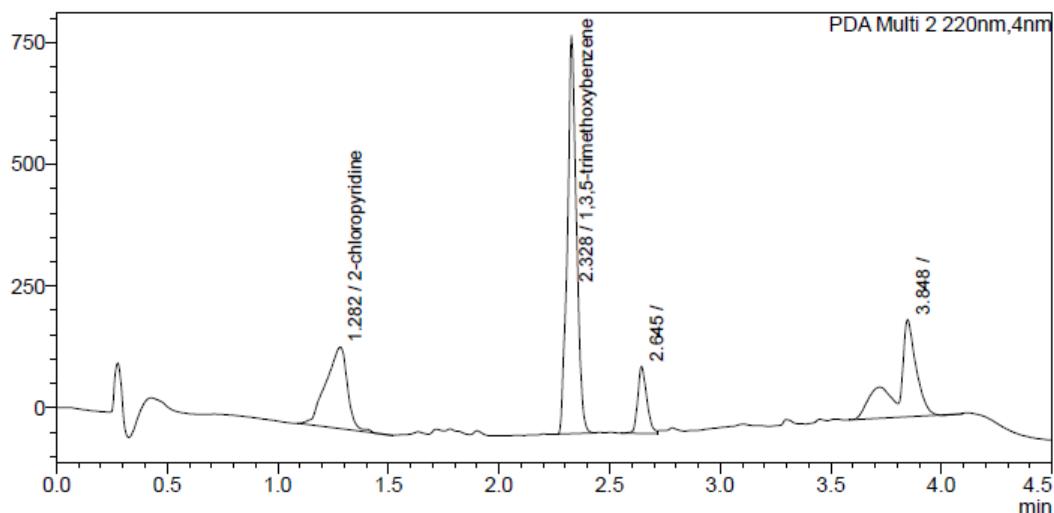


Figure S94. Representative UPLC trace for primary C-N coupling ($\text{Pd}_2\text{dba}_3 \bullet \text{CHCl}_3 / \text{P}(t\text{Bu})_3$)

Table S3. HPLC peak areas for the screen of the primary amine C-N coupling.

Peak Area				
		2-chloropyridine	N-Benzylpyridin-2-amine	1,3,5-trimethoxybenzene
$\text{Pd}(\text{OAc})_2$	BrettPhos	0	3385492	2997690
	Xphos	0	76787	2453649
	<i>t</i> BuXPhos	0	2377402	2655255
	<i>t</i> BuBrettPhos	0	2307905	2515666
	RuPhos	0	1733149	2461734
	$\text{P}(t\text{Bu})_3$	1105874	0	2325394
$[\text{Pd}(\text{allyl})\text{Cl}]_2$	BrettPhos	0	2370577	2334463
	Xphos	0	0	2271905
	<i>t</i> BuXPhos	0	3082567	2454643
	<i>t</i> BuBrettPhos	0	2729767	2434876
	RuPhos	0	1669756	2367546
	$\text{P}(t\text{Bu})_3$	673521	496436	2286357
$\text{Pd}_2\text{dba}_3 \bullet \text{CHCl}_3$	BrettPhos	0	3312089	3317989
	Xphos	0	81863	2288290
	<i>t</i> BuXPhos	0	2837787	2404427
	<i>t</i> BuBrettPhos	0	2952075	2509544
	RuPhos	0	1799661	2353881
	$\text{P}(t\text{Bu})_3$	1125019	0	2336137
$^{\text{DMP}}\text{DAB-Pd-MAH}$	BrettPhos	0	3447511	1976975
	Xphos	0	67808	2158353
	<i>t</i> BuXPhos	0	3283754	1861477
	<i>t</i> BuBrettPhos	0	3397940	1900147
	RuPhos	0	3072338	2358024
	$\text{P}(t\text{Bu})_3$	1019157	185338	1952504

2° Amine C-N

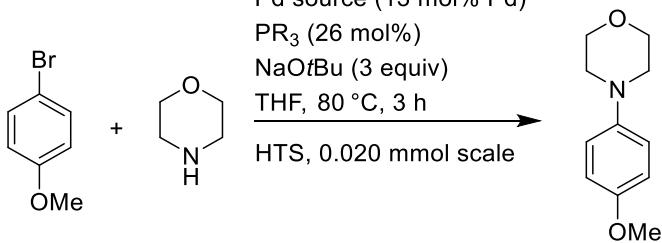


Table S4. UPLC gradient profile in secondary C-N coupling.

Time (min)	Mobile Phase B (ACN) %	Flow Rate (mL/min)	Injection Volume (μL)
0.01	2	0.8	5
0.01-4	2-98		
4-4.1	98-2		
4.1-4.5	2		

mAU

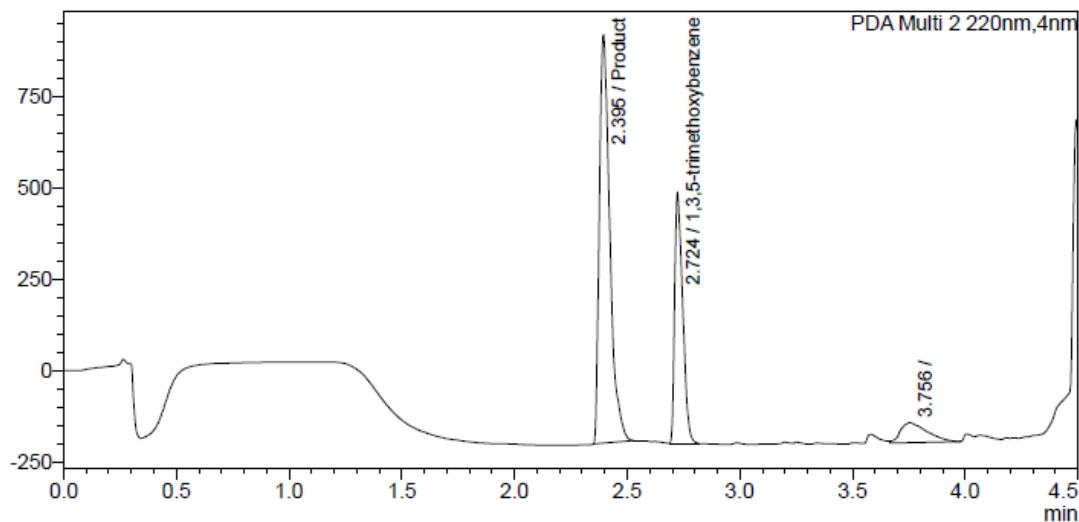


Figure S95. Representative UPLC trace for secondary C-N coupling (^{DMP}DAB-Pd-MAH/RuPhos)

mAU

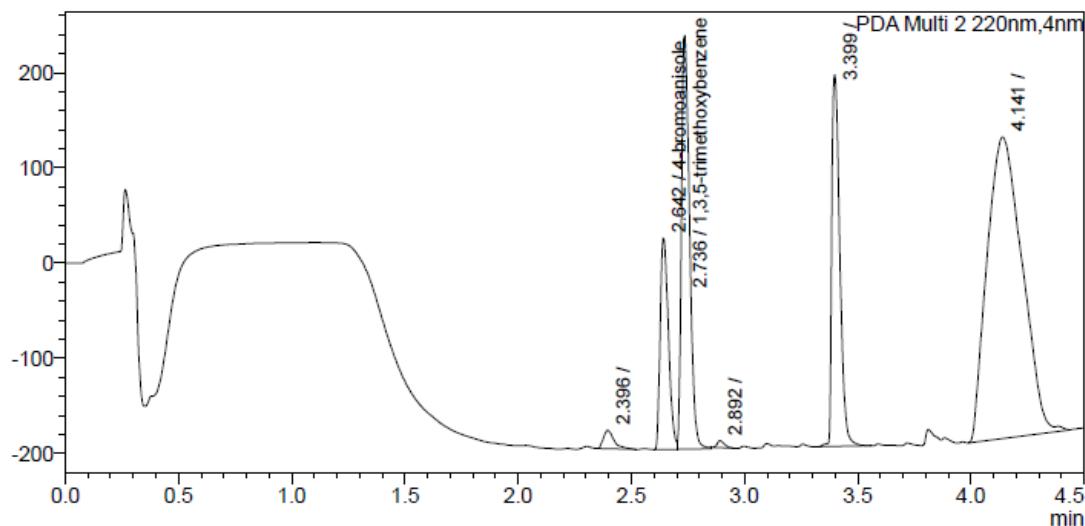


Figure S96. Representative UPLC trace for secondary C-N coupling ($\text{Pd}(\text{OAc})_2/t\text{BuBrettPhos}$)

Table S5. HPLC peak areas for the screen of the secondary C-N coupling.

Peak Area				
		4-bromoanisole	4-(4-Methoxyphenyl)morpholine	1,3,5-trimethoxybenzene
$\text{Pd}(\text{OAc})_2$	BrettPhos	252879	1621663	1155080
	Xphos	48764	2135289	1217403
	<i>t</i> BuXPhos	325613	1327837	1202379
	<i>t</i> BuBrettPhos	563476	0	1079231
	RuPhos	0	2239831	1248760
	P(<i>t</i> Bu)3	33578	2218340	1310637
$[\text{Pd}(\text{allyl})\text{Cl}]_2$	BrettPhos	154978	1962981	1170919
	Xphos	41485	2099868	1125205
	<i>t</i> BuXPhos	26394	2124637	1144206
	<i>t</i> BuBrettPhos	276407	1414466	1205944
	RuPhos	25981	2369094	1279222
	P(<i>t</i> Bu)3	58704	1741241	1143075
$\text{Pd}_2\text{dba}_3 \bullet \text{CHCl}_3$	BrettPhos	194292	1983567	1231454
	Xphos	81890	2597186	1461177
	<i>t</i> BuXPhos	76280	2335810	1430355
	<i>t</i> BuBrettPhos	515913	255223	1233285
	RuPhos	54649	2354111	1304103
	P(<i>t</i> Bu)3	143585	2551969	1763992
$^{\text{DMP}}\text{DAB-Pd-MAH}$	BrettPhos	232626	3141942	1836385
	Xphos	133078	2406601	1295819
	<i>t</i> BuXPhos	38335	3353916	1696089
	<i>t</i> BuBrettPhos	0	1887528	1698093
	RuPhos	0	3602097	1698681
	P(<i>t</i> Bu)3	62502	2763901	1727788

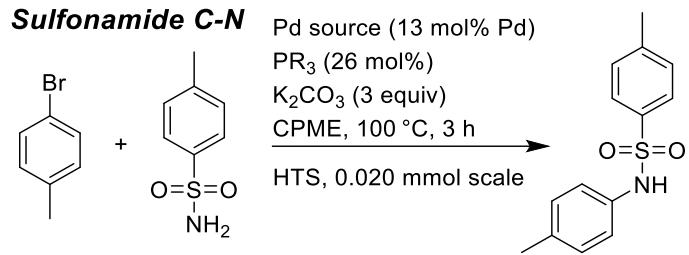


Table S6. UPLC gradient profile in sulfonamide C-N coupling.

Time (min)	Mobile Phase B (ACN) %	Flow Rate (mL/min)	Injection Volume (μL)
0.1	2	1.3	5
0.1-2	2-98		
2-2.1	98-2		
2.1-2.5	2		

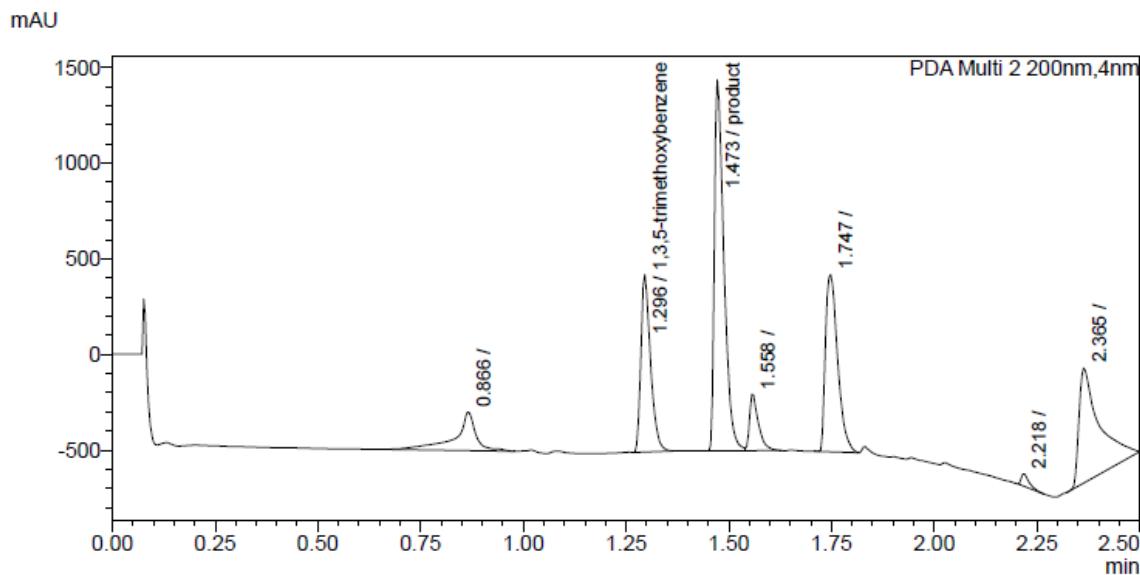
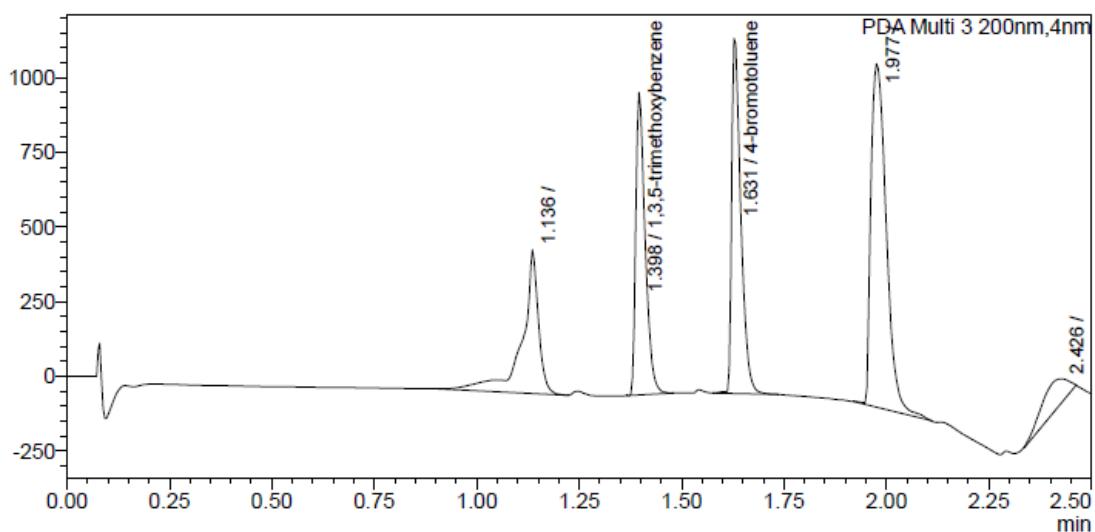


Figure S97. Representative UPLC trace for sulfonamide C-N coupling (${}^{\text{DMP}}\text{DAB-Pd-MAH}/t\text{BuXPhos}$)

mAU

**Figure S98.** Representative UPLC trace for sulfonamide C-N coupling ($\text{Pd}(\text{OAc})_2/\text{Me}_4\text{tBuXPhos}$)**Table S7.** HPLC peak areas for the screen of the sulfonamide C-N coupling.

Peak Area				
		4-bromotoluene	N-(4-Methylphenyl)-4-methylbenzenesulfonamide	1,3,5-trimethoxybenzene
$\text{Pd}(\text{OAc})_2$	XantPhos	828182	286064	1855238
	Xphos	1401321	1248346	1709830
	<i>t</i> BuXPhos	1713058	661591	1674885
	$\text{Me}_4\text{tBuXPhos}$	1842639	0	1612624
	BippyPhos	1894665	635097	1699286
	JackiePhos	1690195*	678312	1715822
$[\text{Pd}(\text{allyl})\text{Cl}]_2$	XantPhos	1490106*	690288	1899480
	Xphos	652314	2282165	1715642
	<i>t</i> BuXPhos	632700	1865855	1714584
	$\text{Me}_4\text{tBuXPhos}$	0	2955988	1715342
	BippyPhos	0	2735683	1759315
	JackiePhos	0	2769710	1738446
$\text{Pd}_{\text{dba}}_3 \bullet \text{CHCl}_3$	XantPhos	1498090	461837	1906187
	Xphos	704468	2497133	1682254
	<i>t</i> BuXPhos	953414	2324289	1703807
	$\text{Me}_4\text{tBuXPhos}$	482981	2589245	1615176
	BippyPhos	149533*	2941408	1712223
	JackiePhos	0	2581352	1683564
$^{\text{DMP}}\text{DAB-Pd-MAH}$	XantPhos	1527896	670644	2020114
	Xphos	1629389	993276	1805830
	<i>t</i> BuXPhos	0	3130626	1505343
	$\text{Me}_4\text{tBuXPhos}$	1000338	2362555	1691062
	BippyPhos	1484447	1467249	1753619
	JackiePhos	1544264	1423967	1499409

*: The peak overlaps with other peaks

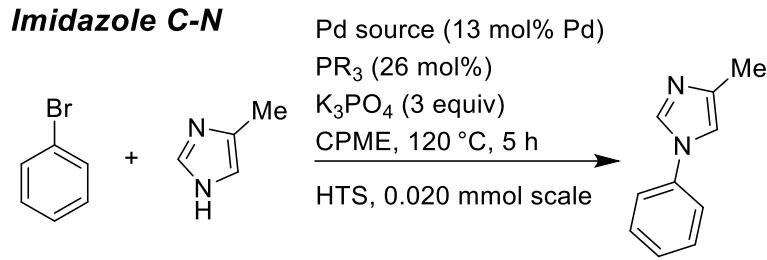


Table S8. UPLC gradient profile in imidazole C-N coupling.

Time (min)	Mobile Phase B (ACN) %	Flow Rate (mL/min)	Injection Volume (μL)
0.01	2	0.8	10
0.01-8	2-70		
8.0-10	70		
10-10.1	70-2		
10.1-12	2		

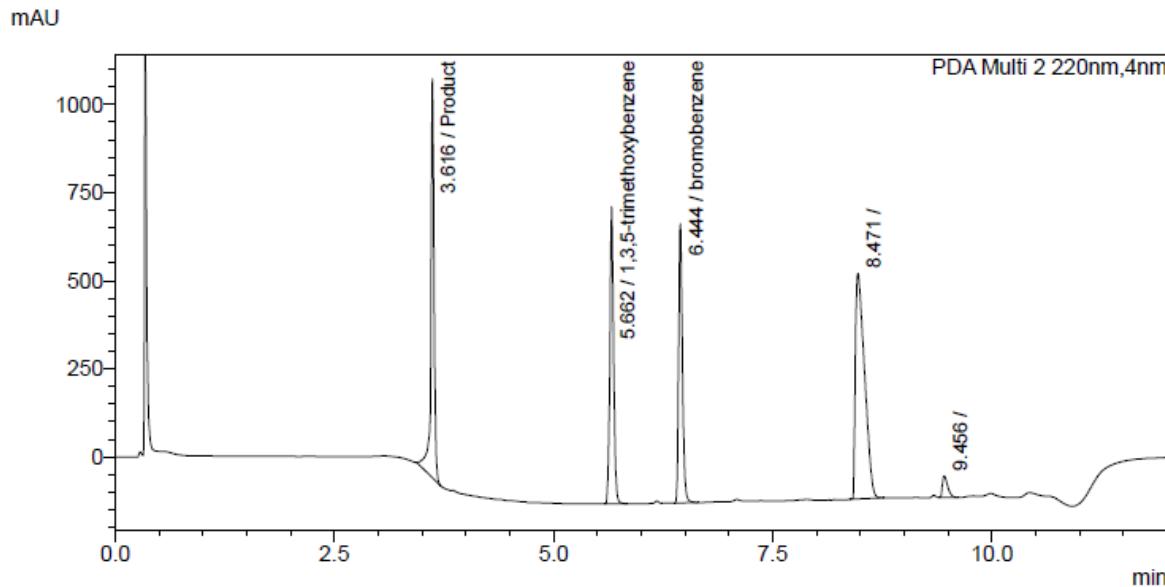
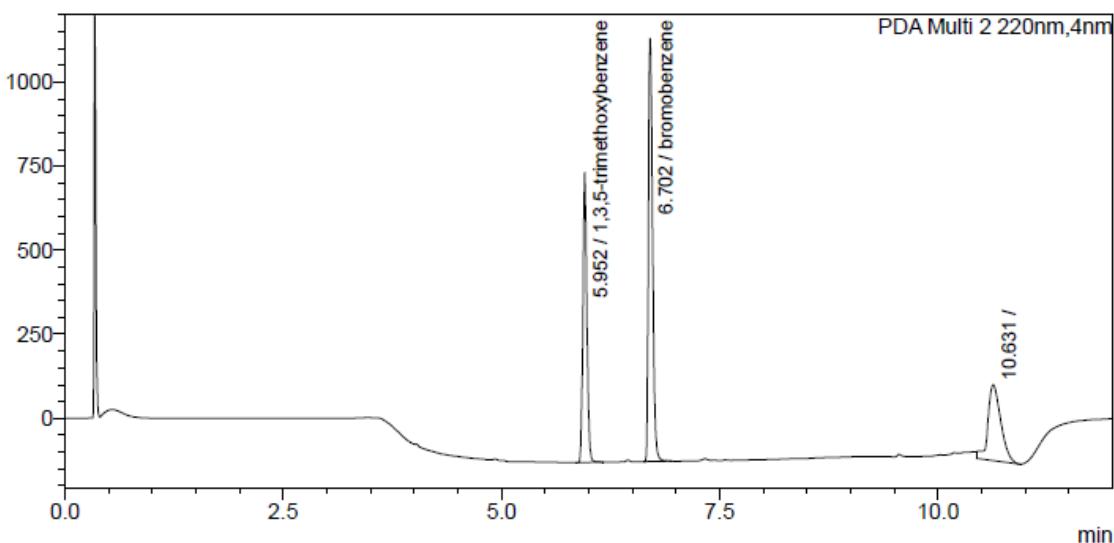


Figure S99. Representative UPLC trace for imidazole C-N coupling (${}^{\text{DMP}}\text{DAB-Pd-MAH/tBuBrettPhos}$)

mAU

**Figure S100.** Representative UPLC trace for imidazole C-N coupling ($[\text{Pd}(\text{allyl})\text{Cl}]_2/\text{XPhos}$)**Table S9.** HPLC peak areas for the screen of the imidazole C-N coupling.

Peak Area				
		bromobenzene	4-methyl-1-phenyl-1H-imidazole	1,3,5-trimethoxybenzene
$\text{Pd}(\text{OAc})_2$	BrettPhos	4902673	0	2908775
	Xphos	4571225	0	2693832
	<i>t</i> BuXPhos	4308077	50036	2570979
	<i>t</i> BuBrettPhos	4373545	25038	2669042
	$\text{Me}_4\text{tBuXPhos}$	4417449	0	2600933
	BippyPhos	4631296	0	2800852
$[\text{Pd}(\text{allyl})\text{Cl}]_2$	BrettPhos	4125483	90172	2707002
	Xphos	4220220	0	2700361
	<i>t</i> BuXPhos	1439335	0	3221589
	<i>t</i> BuBrettPhos	2972207	1298343	3756382
	$\text{Me}_4\text{tBuXPhos}$	3519533	780383	2561988
	BippyPhos	4251645	0	2604595
$\text{Pd}_2\text{dba}_3 \bullet \text{CHCl}_3$	BrettPhos	4190279	119157	2736082
	Xphos	4025391	0	2568351
	<i>t</i> BuXPhos	3323695	178714	2536932
	<i>t</i> BuBrettPhos	2108103	2218445	2611913
	$\text{Me}_4\text{tBuXPhos}$	2792228	1376263	2514431
	BippyPhos	1248583	0	4432359
^{DMP} DAB-Pd-MAH	BrettPhos	4364954	488724	2711391
	Xphos	4129583	300332	2514790
	<i>t</i> BuXPhos	3361859	1031999	2484008
	<i>t</i> BuBrettPhos	2354270	2844027	2472766
	$\text{Me}_4\text{tBuXPhos}$	3796109	1193196	2944526
	BippyPhos	4106500	327324	2504938

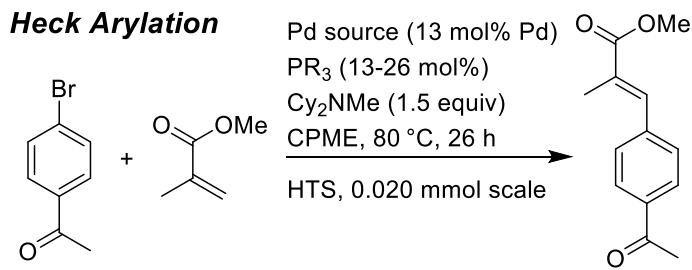


Table S10. UPLC gradient profile in Heck arylation.

Time (min)	Mobile Phase B (ACN) %	Flow Rate (mL/min)	Injection Volume (μL)
0.01	2	0.8	4
0.01-10	2-60		
10-10.1	60-2		
10.1-12.5	2		

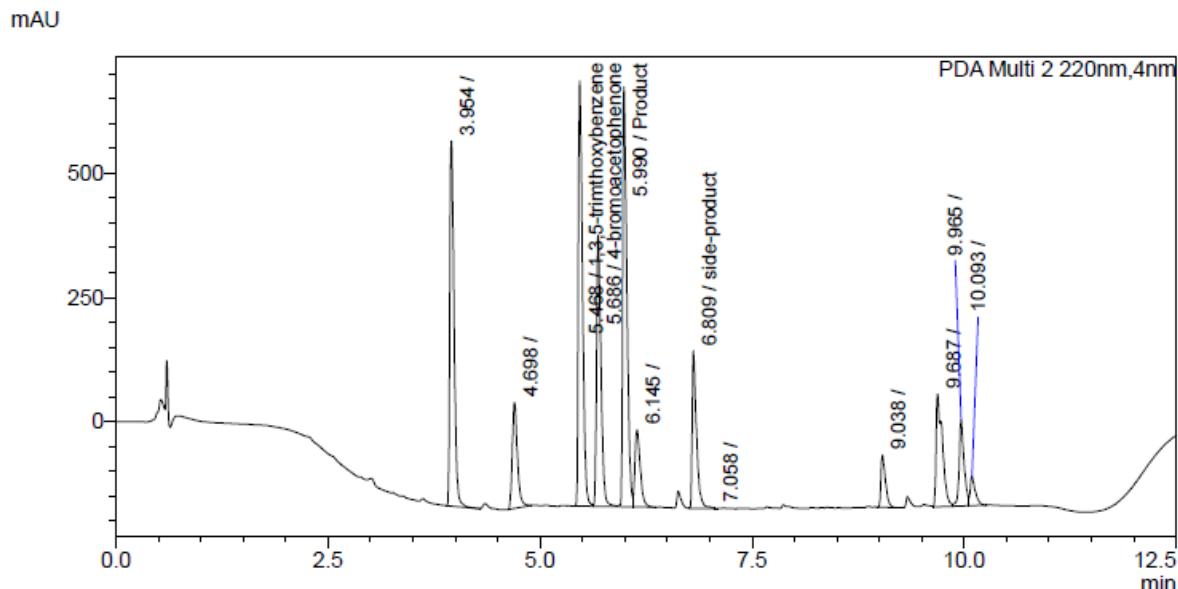
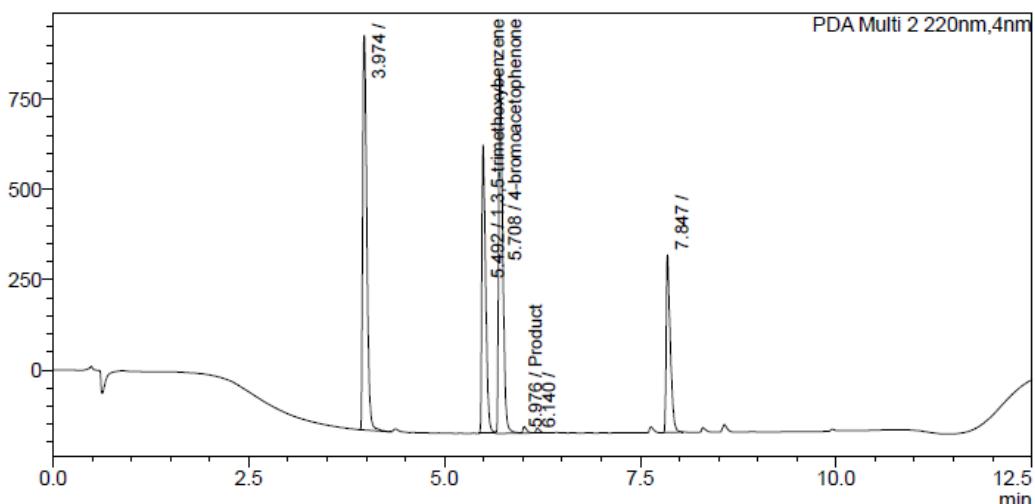


Figure S101. Representative UPLC trace for Heck arylation (${}^{\text{DMP}}\text{DAB-Pd-MAH/P(tBu)}_3$)

mAU

**Figure S102.** Representative UPLC trace for Heck arylation ($\text{Pd}_2\text{dba}_3 \bullet \text{CHCl}_3 / \text{P}(\text{Cy})_3$)**Table S11.** HPLC peak areas for the screen of the Heck arylation.

Peak Area				
		4-bromoacetophenone	(E)-3-(4-acetylphenyl)-2-methyl acrylic acid methyl ester	1,3,5-trimethoxybenzene
$\text{Pd}(\text{OAc})_2$	P(Cy)3	3697354	0	2713253
	Xphos	3133597	1010419	2705608
	P(<i>o-tol</i>)3	4054456	0	2665803
	cataCXium A	3648619	0	2750180
	dppp	5046162*	613668	2780601
	P(<i>tBu</i>)3	3877056	0	2863547
$[\text{Pd}(\text{allyl})\text{Cl}]_2$	P(Cy)3	3990226	0	2714838
	Xphos	4011877	0	2712272
	P(<i>o-tol</i>)3	3372182	1386149	2593248
	cataCXium A	3615156	0	2716009
	dppp	4262695*	0	2754042
	P(<i>tBu</i>)3	289680	4093293	2804407
$\text{Pd}_2\text{dba}_3 \bullet \text{CHCl}_3$	P(Cy)3	3652851	5205	2726519
	Xphos	3269325	983800	2707691
	P(<i>o-tol</i>)3	2154853	2455809	2721192
	cataCXium A	3575334	0	2700032
	dppp	5268009*	0	2695499
	P(<i>tBu</i>)3	175305	4021632	2785341
^{DMP} DAB-Pd-MAH	P(Cy)3	3934671	0	2821811
	Xphos	4098690	0	2776081
	P(<i>o-tol</i>)3	3695598*	1178678	2804769
	cataCXium A	3835483	0	2899726
	dppp	6550918*	0	2797375
	P(<i>tBu</i>)3	1977407	2894277	2934081

*: The peak overlaps with other peaks.

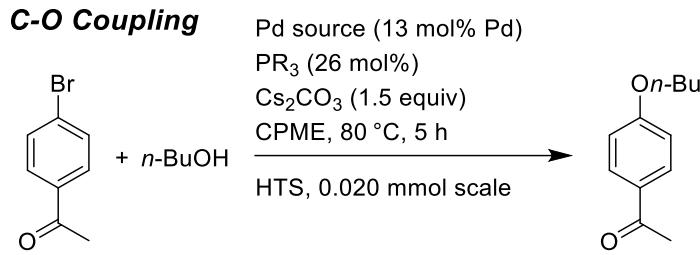


Table S12. LC gradient profile 1 in C-O coupling.

Time (min)	Mobile Phase A %	Mobile Phase B %	Flow Rate (mL/min)	Injection Volume (μL)
initial	90	10	0.5	2
1	90	10		
6.5	10	90		
8	10	90		
8.1	90	10		
10	90	10		

Table S13. LC gradient profile 2 in C-O coupling.

Time (min)	Mobile Phase A %	Mobile Phase B %	Flow Rate (mL/min)	Injection Volume (μL)
initial	90	10	0.5	2
1	90	10		
3	10	90		
4	10	90		
4.01	90	10		
5	90	10		

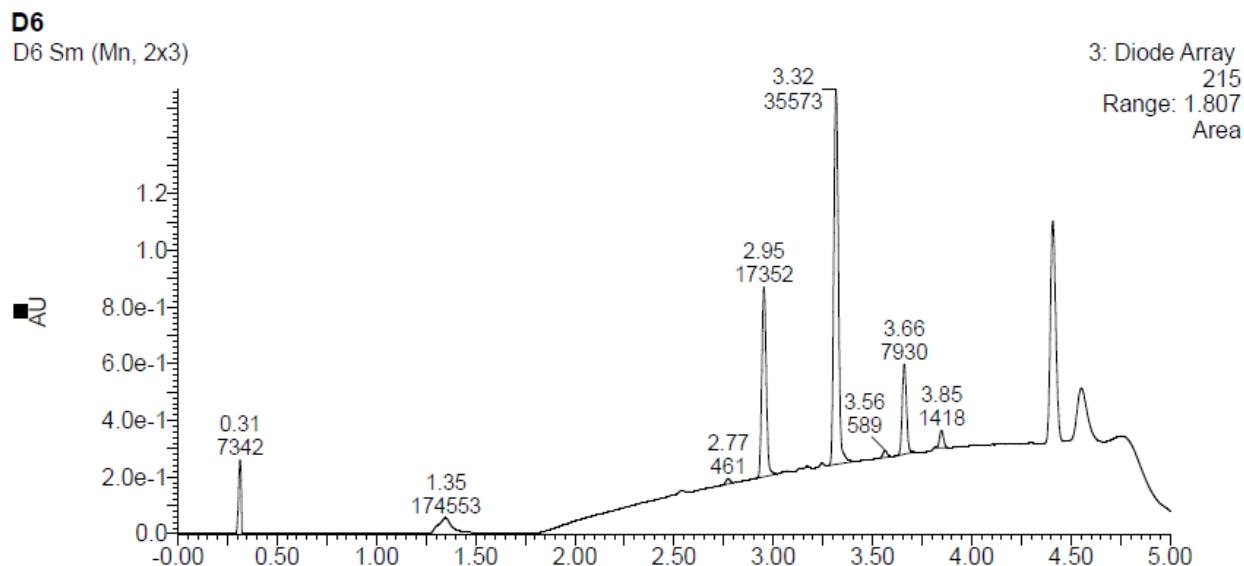
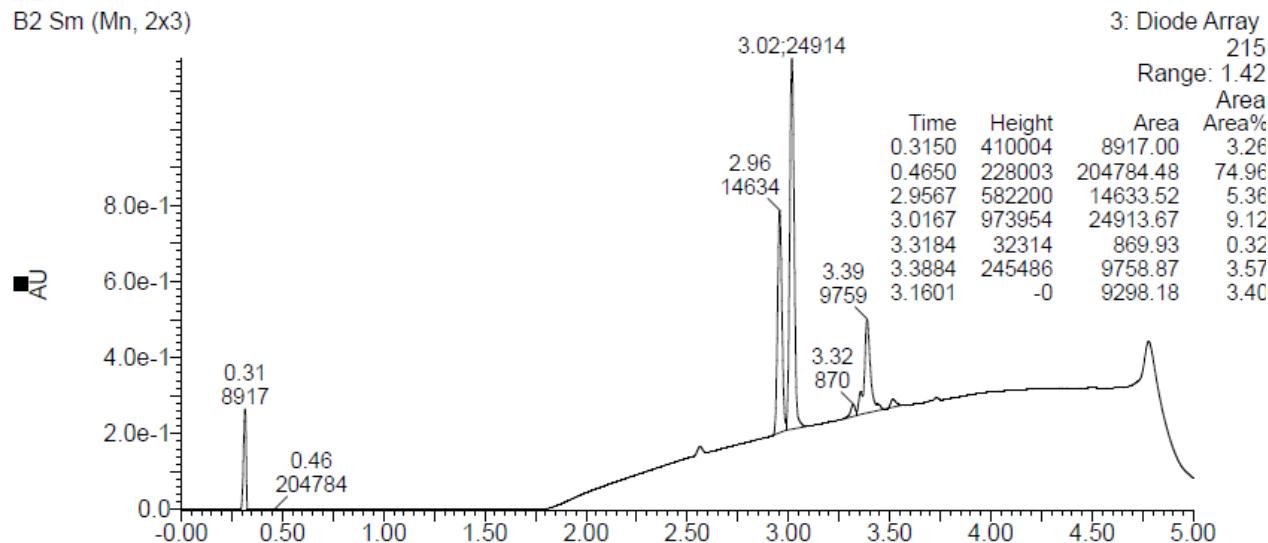


Figure S103. Representative LC-MS trace for C-O coupling ($^{\text{DMP}}$ DAB-Pd-MAH/BippyPhos)

B2

B2 Sm (Mn, 2x3)

**Figure S104.** Representative LC-MS trace for C-O coupling ($[Pd(allyl)Cl]_2/XPhos$)**Table S14.** HPLC peak areas for the screen of the C-O coupling.

Peak Area				
		4-bromoacetophenone	1-(4-n-Butoxyphenyl)ethanone	1,3,5-trimethoxybenzene
$Pd(OAc)_2$	BrettPhos	0	16394	9937
	Xphos	0	4796	16462
	tBuXPhos	3431	3294	3249
	tBuBrettPhos	8133	24288	17588
	Me ₄ tBuXPhos	0	21140	15193
	BippyPhos	0	33879	16345
$[Pd(allyl)Cl]_2$	BrettPhos	0	24797	15639
	Xphos	24914	870	14634
	tBuXPhos	17478	7831	18873
	tBuBrettPhos	9261	9856	18759
	Me ₄ tBuXPhos	11568	12345	18724
	BippyPhos	16455	12421	16929
$Pd_2dba_3 \bullet CHCl_3$	BrettPhos	0	26791	15385
	Xphos	2122	4430	15765
	tBuXPhos	6607	20584	14592
	tBuBrettPhos	4168	23313	16532
	Me ₄ tBuXPhos	3077	15562	15412
	BippyPhos	0	28533	15741
^{DMP} DAB-Pd-MAH	BrettPhos	3675	21248	12767
	Xphos	12303	3776	15751
	tBuXPhos	18218	15658	15632
	tBuBrettPhos	9388	19751	15729
	Me ₄ tBuXPhos	14421	13669	15527
	BippyPhos	0	35573	17352

spiro-OMeTAD Synthesis

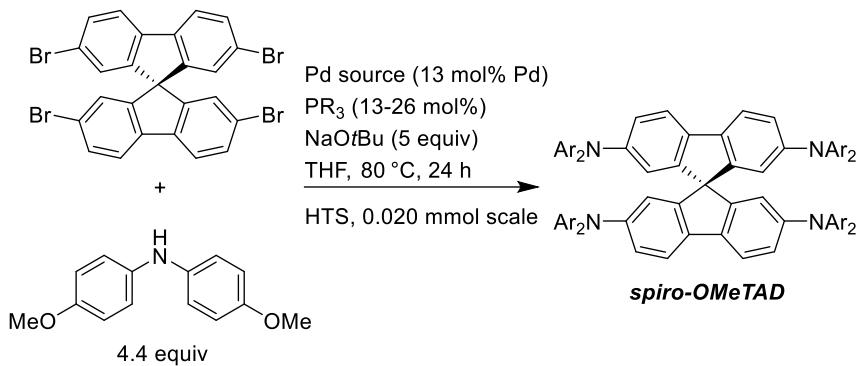


Table S15. UPLC gradient profile in the synthesis of *spiro*-OMeTAD.

Time (min)	Mobile Phase B (ACN) %	Flow Rate (mL/min)	Injection Volume (μL)
0.01	30	0.8	2
0.01-10	30-95		
10-13.4	95		
13.4-13.5	95-30		

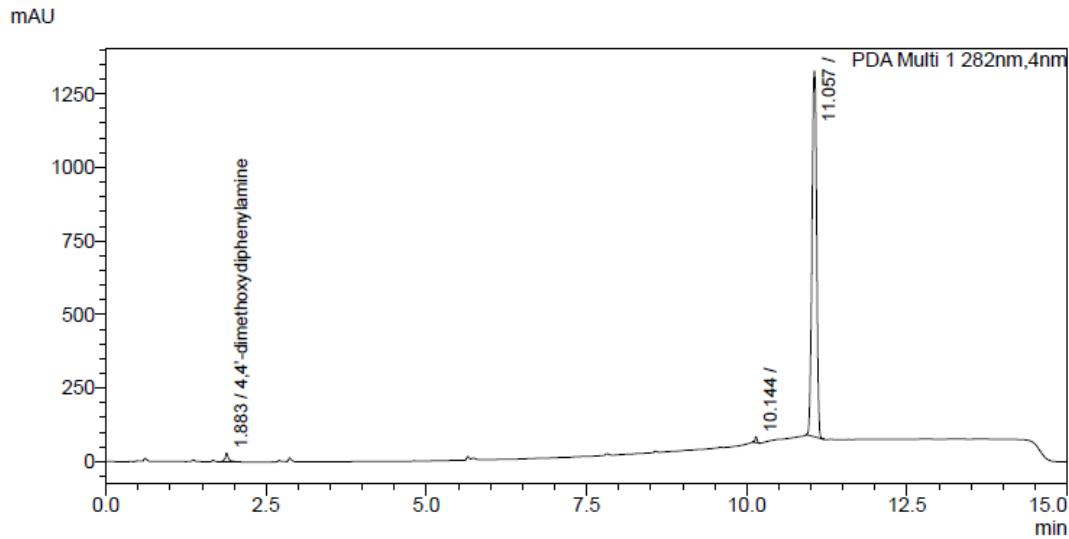


Figure S105. Representative UPLC trace for synthesis of *spiro*-OMeTAD at 282 nm (^{DMP}DAB-Pd-MAH/XPhos)

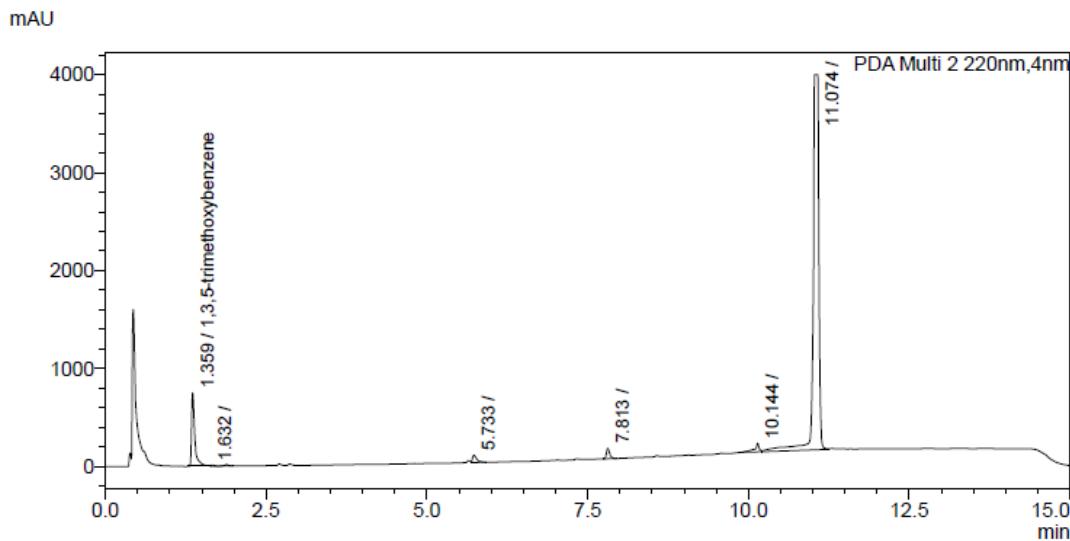


Figure S106. Representative UPLC trace for synthesis of *spiro*-OMeTAD at 220 nm (^{DMP}DAB-Pd-MAH/XPhos)

Table S16. HPLC peak areas for the screen of the synthesis of spiro-OMeTAD.

Peak Area				
		4,4'-dimethoxydiphenylamine	Spiro-OMeTAD	1,3,5-trimethoxybenzene
^{DMP} DAB-Pd-MAH	BrettPhos	7284590	3866889	3648099
	Xphos	116877	9326234	2570339
	tBuXPhos	3145161	4339269	2431577
	Sphos	349246	7523095	2457494
	RuPhos	1396243	7727987	2609098
	XantPhos	1739682	8708891	2588164

IV: Preparative-Scale Synthesis

N-Benzylpyridin-2-amine

A 4-dram vial was charged with 2-chloropyridine (426 μL , 4.50 mmol), benzylamine (590 μL , 5.40 mmol), NaOt-Bu (519 mg, 5.40 mmol), **1** (5.3 mg, 0.0113 mmol), BrettPhos (12.1 mg, 0.0225 mmol), and 9 mL of THF. The mixture was stirred at 60 °C for 1 h. Ethyl acetate was added to dilute the reaction mixture, and the diluted mixture was washed three times with water, dried over Mg₂SO₄ anhydrous and concentrated in the rotary evaporator. Finally, the crude product was dried in the vacuo to give 755 mg (4.10 mmol, 91%) product as a light yellow solid. Spectroscopic data is consistent with reported values.⁵ ¹H NMR (300 MHz, CDCl₃): δ 8.11 (d, J = 4.0 Hz, 1H), 7.38 (m, 5H), 7.27 (m, 1H), 6.59 (m, 1H), 6.38 (d, J = 8.4 Hz, 1H), 4.92 (br, 1H), 4.51 (d, J = 5.8 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃): δ 158.7, 148.2, 139.2, 137.5, 128.6, 127.4, 127.2, 113.1, 106.8, 46.3.

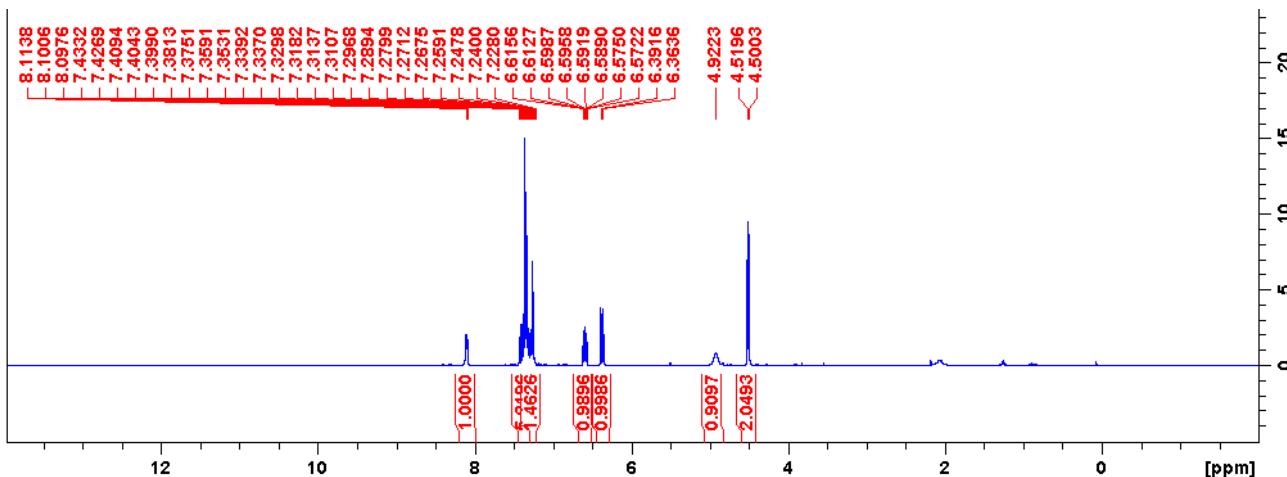
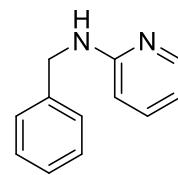


Figure S107. ¹H NMR spectrum (300 MHz; CDCl₃) of N-benzylpyridin-2-amine

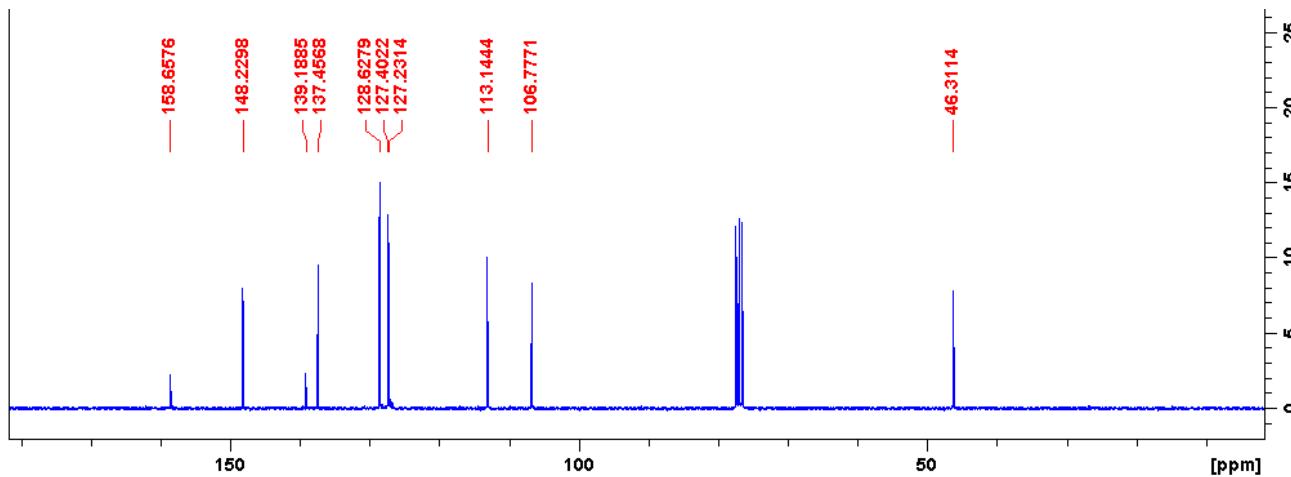


Figure S108. ¹³C{¹H} NMR spectrum (75 MHz; CDCl₃) of N-benzylpyridin-2-amine

4-(4-Methoxyphenyl)morpholine

A 4-dram vial was charged with 4-bromoanisole (128 μL , 1.00 mmol), morpholine (106 μL , 1.20 mmol), NaOt-Bu (116 mg, 1.20 mmol), **1** (9.4 mg, 0.02 mmol), RuPhos (18.7 mg, 0.04 mmol), and 2 mL of THF. The mixture was stirred at 80 °C for 2 h. Ethyl acetate was added to dilute the reaction mixture, and the diluted mixture was washed three times with water, dried over Mg_2SO_4 anhydrous and concentrated in the vacuo overnight to give 155.1 mg (0.92 mmol, 92%) product as a yellow solid. Spectroscopic data is consistent with reported values. ^1H NMR (300 MHz, CDCl_3): δ 6.87 (m, 4H), 3.84 (appt, $J = 4.8$ Hz, 4H), 3.77 (s, 3H), 3.04 (appt, $J = 4.8$ Hz, 4H). ^{13}C NMR (75 MHz, CDCl_3): δ 154.0, 145.6, 117.8, 114.5, 67.0, 55.5, 50.8.

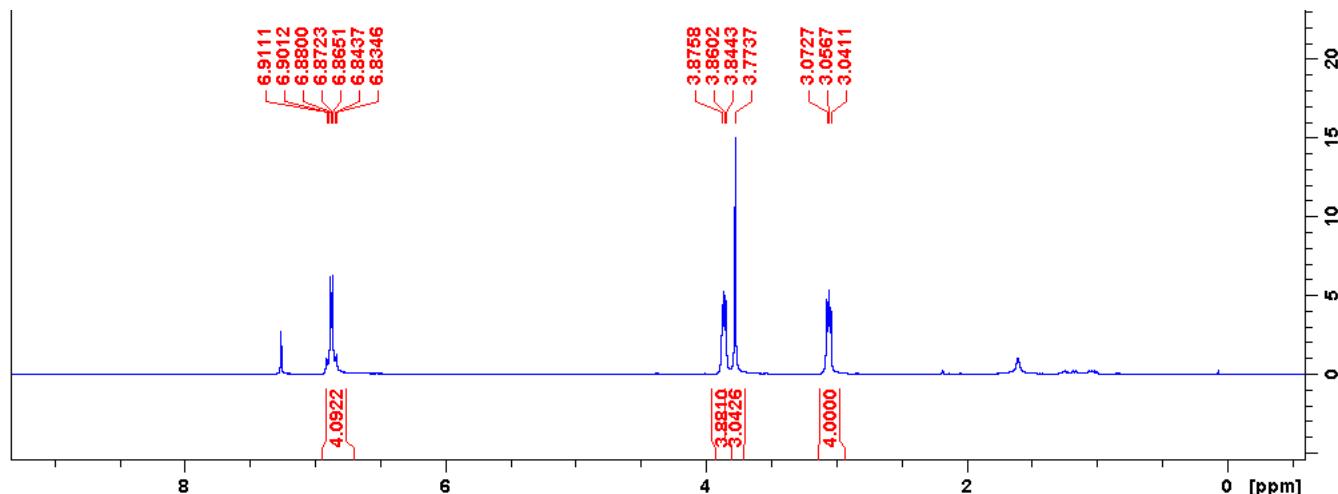
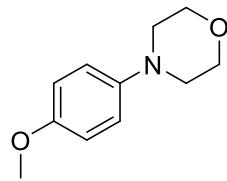


Figure S109. ^1H NMR spectrum (300 MHz; CDCl_3) of 4-(4-methoxyphenyl)morpholine

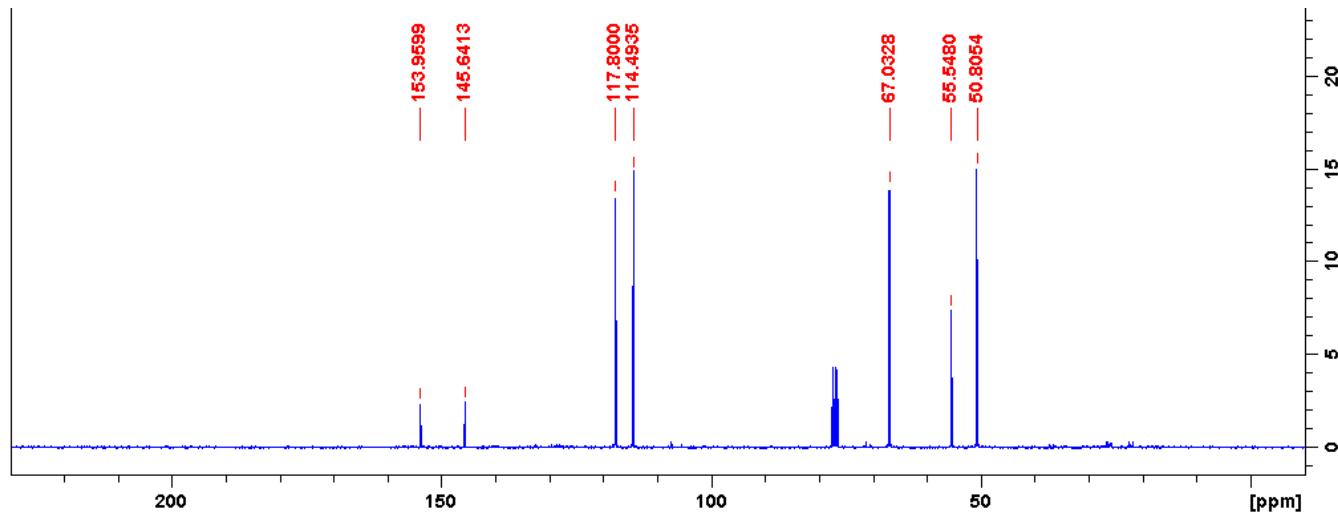


Figure S110. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (75 MHz; CDCl_3) of 4-(4-methoxyphenyl)morpholine

N-(4-Methylphenyl)-4-methylbenzenesulfonamide

A 4-dram vial was charged with 4-bromotoluene (205 mg, 1.20 mmol), p-toluenesulfonamide (172 mg, 1.00 mmol), K_2CO_3 (415 mg, 3.00 mmol), **1** (23.4 mg, 0.05 mmol), *t*BuXPhos (42.5 mg, 0.10 mmol), and 4 mL of CPME. The mixture was stirred at 100 °C for 16 h. Ethyl acetate was added to dilute the reaction mixture, and the diluted mixture was washed three times with water, dried over $MgSO_4$ anhydrous and concentrated in the Genevac. The crude product was purified via a silica plug (DCM/TBME, 20:1) and dried over the Na_2SO_4 to give 183.7 mg (0.70 mmol, 70%) sulfate product as a pale yellow powder. Spectroscopic data is consistent with reported values.⁷ 1H NMR (300 MHz, $CDCl_3$): δ 2.27 (s, 3H), 2.40 (s, 3H), 6.31 (br, 1H), 6.91 (d, J = 8.4 Hz, 2H), 7.04 (d, J = 8.3 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 8.3 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.7, 136.0, 135.0, 134.0, 129.6, 127.3, 122.0, 21.5, 20.8.

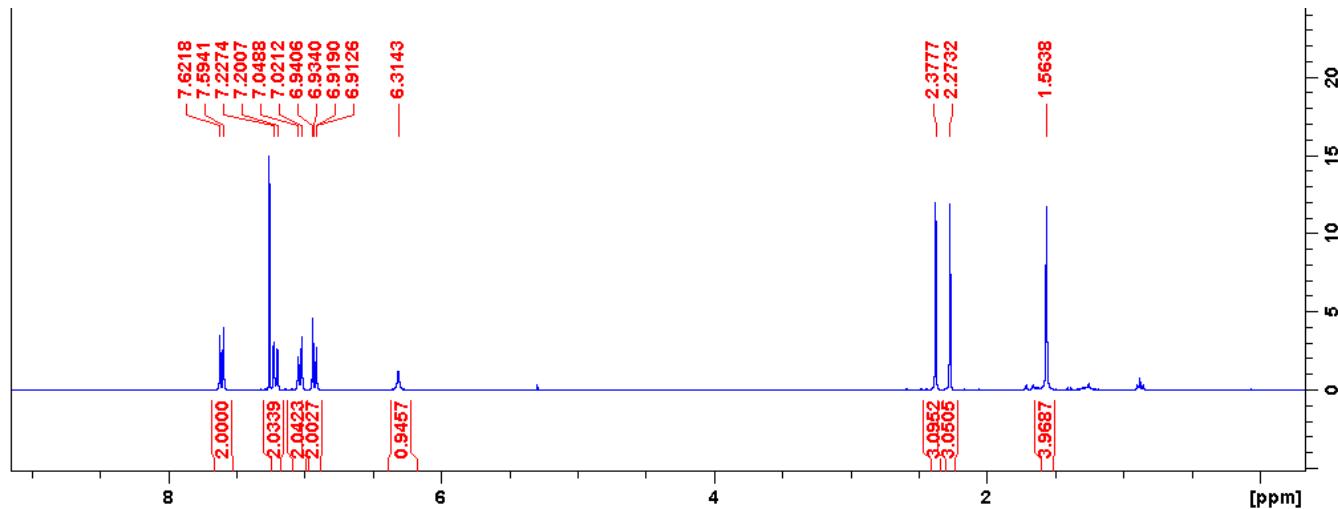
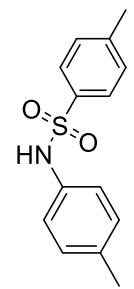


Figure S111. 1H NMR spectrum (300 MHz; $CDCl_3$) of N-(4-methylphenyl)-4-methylbenzenesulfonamide

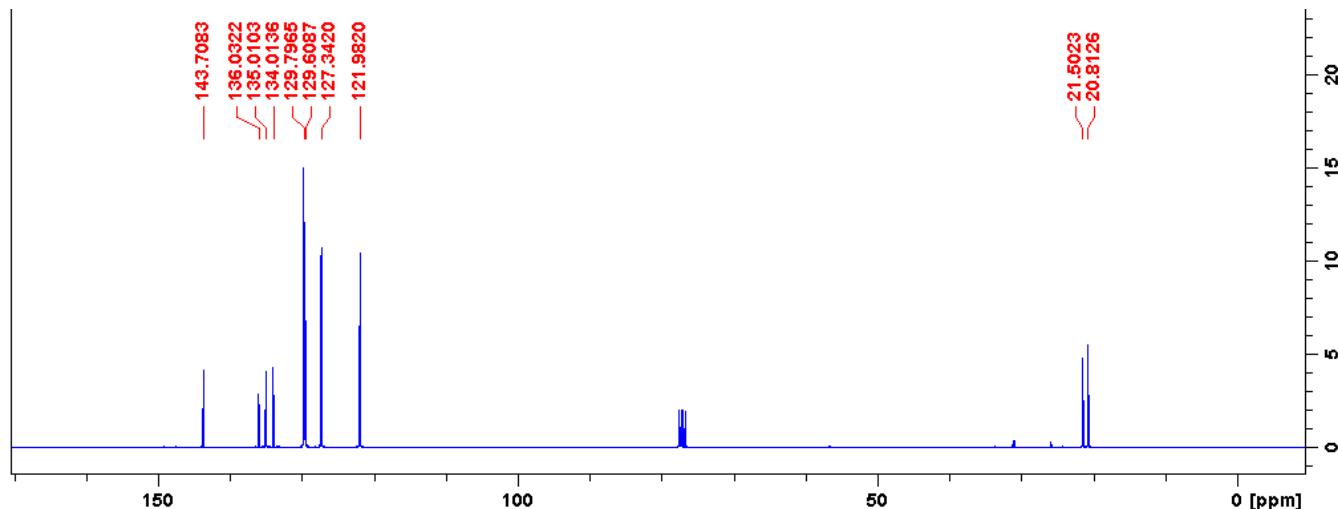


Figure S112. $^{13}C\{^1H\}$ NMR spectrum (75 MHz; $CDCl_3$) of N-(4-methylphenyl)-4-methylbenzenesulfonamide

4-Methyl-1-phenyl-1H-imidazole

A 4-dram vial was charged with bromobenzene (106 μ L, 1.00 mmol), 4-methylimidazole (99 mg, 1.20 mmol), K_3PO_4 (425 mg, 2.00 mmol), **13** (10.3 mg, 0.015 mmol), and 1 mL of CPME. The mixture was stirred at 120 °C for 5 h. The mixture was extracted by DCM and concentrated *in vacuo*. The crude product was purified via flash chromatography (ethyl acetate/hexane, 1:1) to give 101.1 mg (0.64 mmol, 64%) product as a pale yellow solid. Spectroscopic data is consistent with reported values.⁸ 1H NMR (300 MHz, $CDCl_3$): δ 7.76 (d, J = 1.6 Hz, 1H), 7.49-7.44 (m, 2H), 7.37-7.31 (m, 3H), 7.01 (s, 1H), 2.30 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 139.5, 137.4, 134.5, 129.8, 127.0, 121.0, 114.5, 13.7.

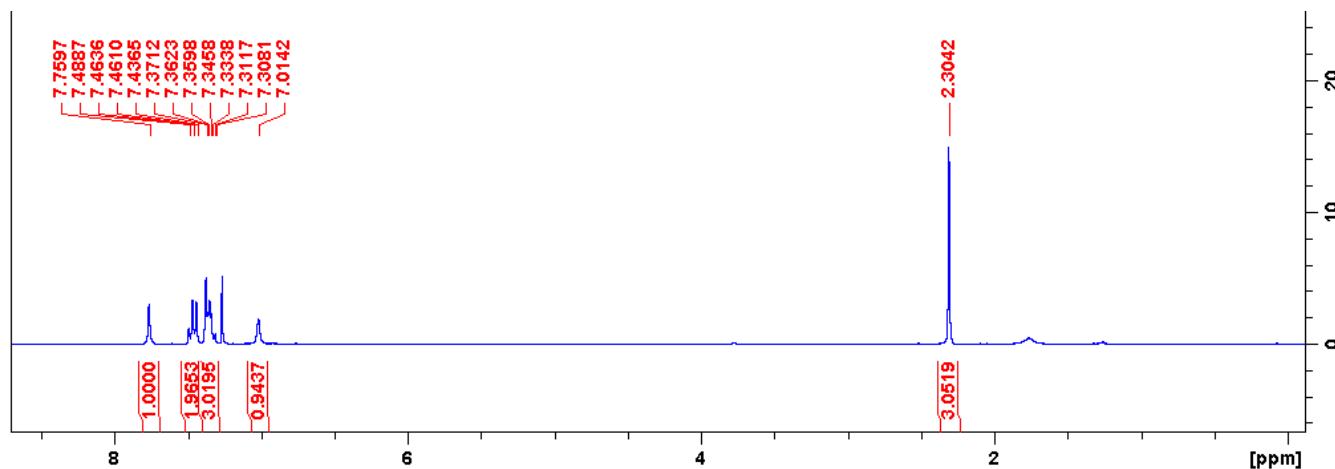
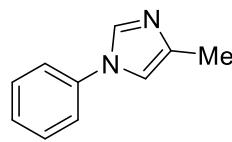


Figure S113. 1H NMR spectrum (300 MHz; $CDCl_3$) of 4-methyl-1-phenyl-1H-imidazole

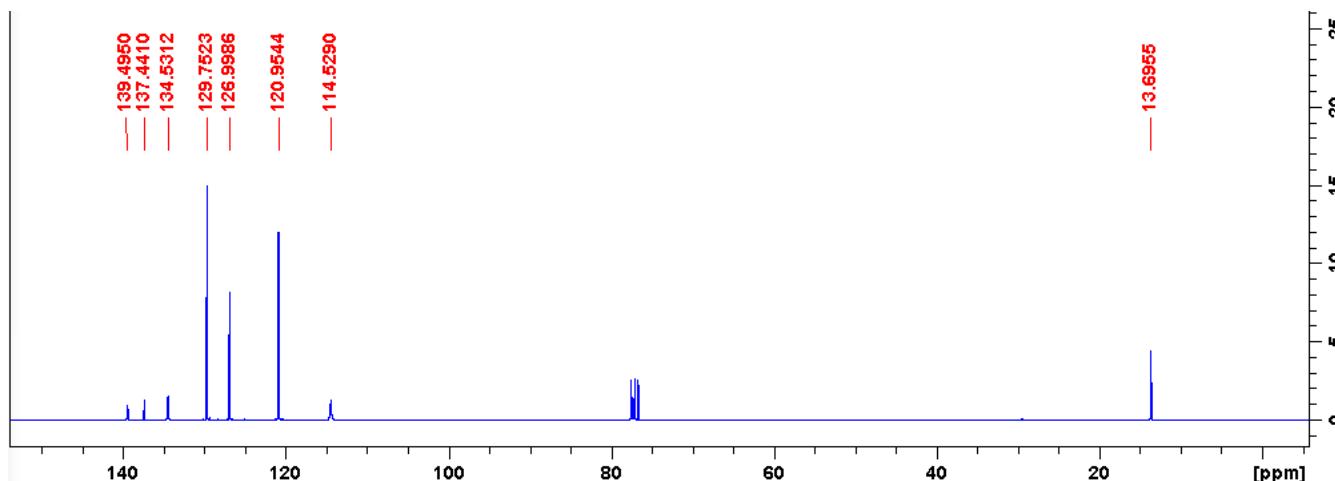


Figure S114. $^{13}C\{^1H\}$ NMR spectrum (75 MHz; $CDCl_3$) of 4-methyl-1-phenyl-1H-imidazole

(E)-3-(4-Acetylphenyl)-2-methyl Acrylic Acid Methyl Ester

A 4-dram vial was charged with 4-bromoacetophenone (185 mg, 0.93 mmol), methyl methacrylate (300 μ L, 2.78 mmol), Cy₂NMe (220 μ L, 1.03 mmol), **1** (4.5 mg, 0.0095 mmol), P(tBu)₃ (4.5 μ L, 0.0095 mmol) and 0.84 mL of CPME. The mixture was stirred at 80 °C for 26 h. The mixture was extracted by DCM and washed by 1M HCl and water, followed by the drying over the MgSO₄. The filtrate was concentrated to give 142.5 mg (0.65 mmol, 76%) product as a light brown solid. Spectroscopic data is consistent with reported values.⁹ ¹H NMR (300 MHz, CDCl₃): δ 7.98 (d, J = 8.4 Hz, 2H), 7.70 (apparent s, 1H), 7.46 (d, J = 8.3 Hz, 2H), 3.83 (s, 3H), 2.62 (s, 3H), 2.12 (d, J = 1.5 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃): δ 197.3, 168.6, 140.4, 137.5, 136.3, 130.3, 129.6, 128.3, 52.2, 26.6, 14.1. NMR spectroscopy (Figure S115, S116) and LCMS (Figure S117) reveals the presence of the bis(arylated) side product (15% by ¹H NMR relative integration).

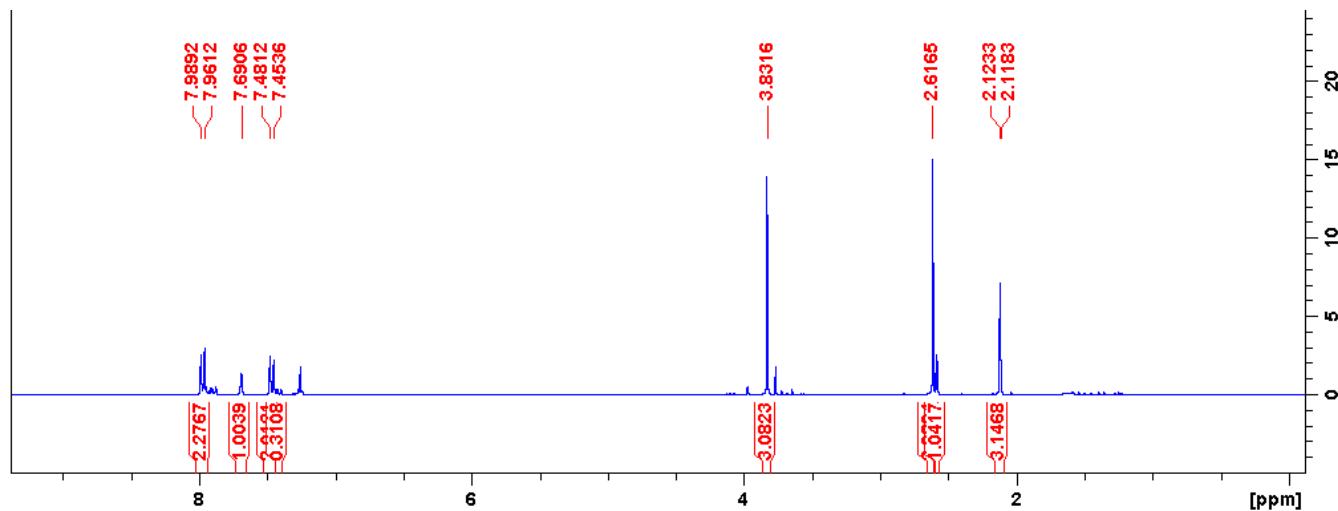
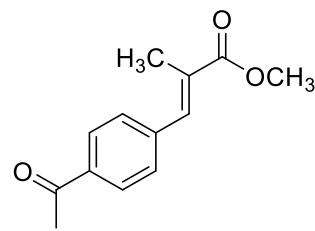


Figure S115. ¹H NMR spectrum (300 MHz; CDCl₃) of (E)-3-(4-acetylphenyl)-2-methyl acrylic acid methyl ester

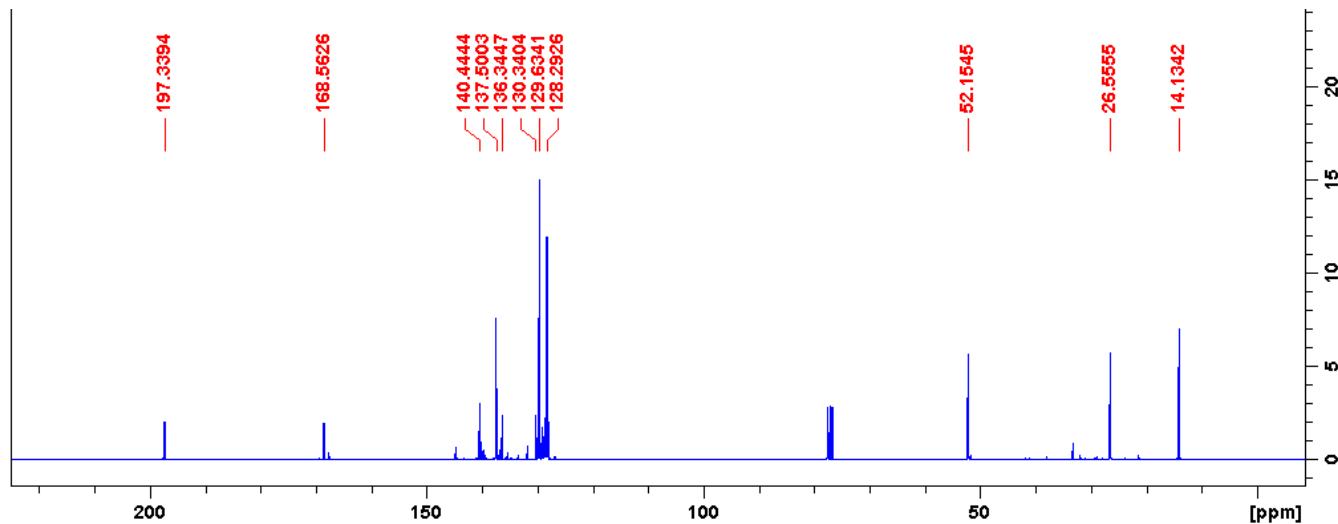


Figure S116. ¹³C{¹H} NMR spectrum (75 MHz; CDCl₃) of (E)-3-(4-acetylphenyl)-2-methyl acrylic acid methyl ester

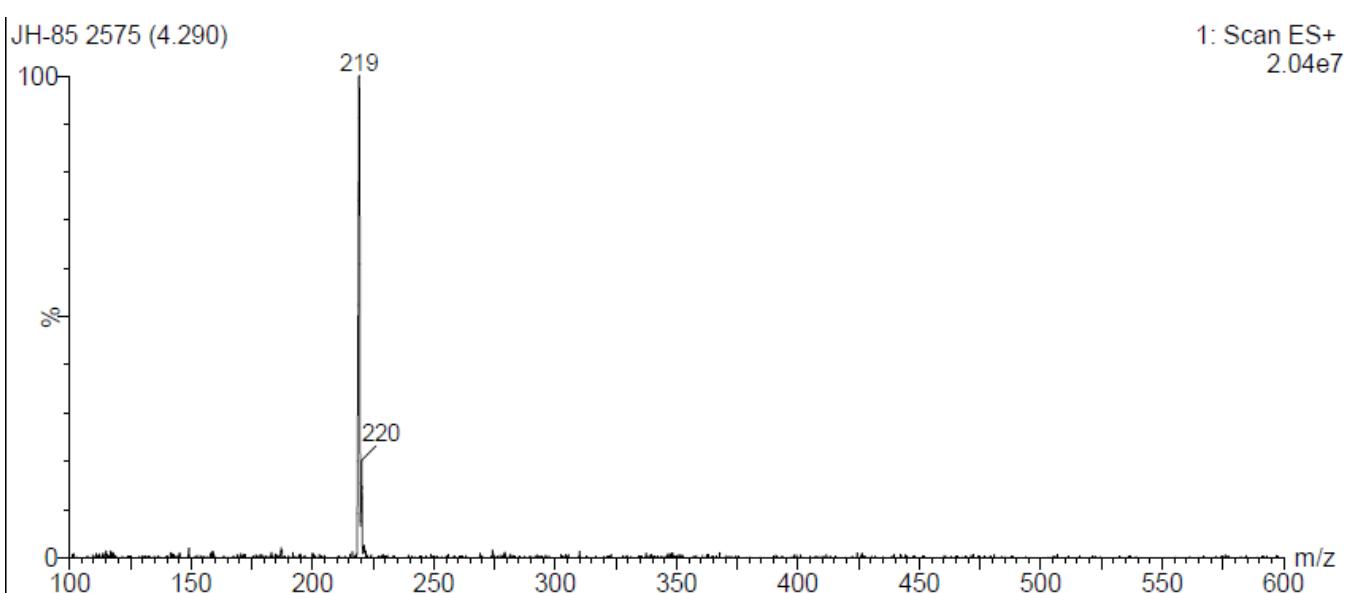
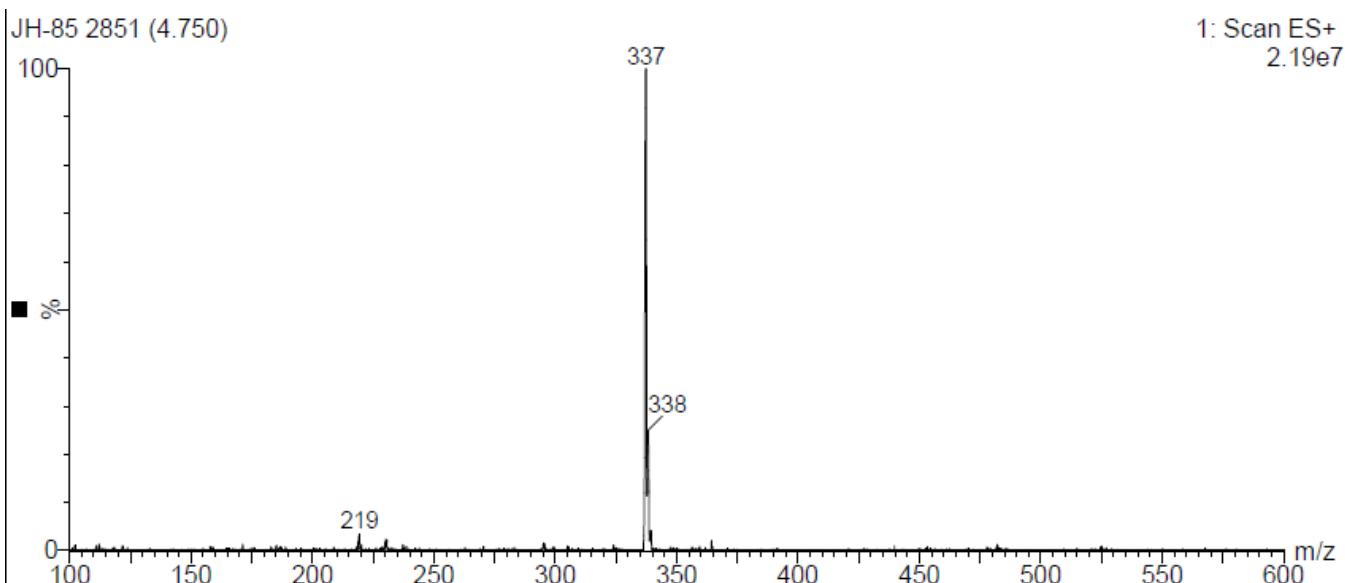


Figure S117. MS (ESI) data from LCMS of isolated product mixture confirming presence of bis(arylation) product (minor, top) and mono(arylation) product (major, bottom).

1-(4-n-Butoxyphenyl)ethanone

A 4-dram vial was charged with 4-bromoacetophenone (199 mg, 1.00 mmol), butyl alcohol (275 μ L, 3.00 mmol), Cs_2CO_3 (489 mg, 1.50 mmol), **1** (4.7 mg, 0.01 mmol), *t*BuBippyPhos (10.1 mg, 0.02 mmol), and 1.8 mL of CPME. The mixture was stirred at 80 °C for 18 h. The mixture was extracted by ethyl acetate and washed three times with water. The organic layer was combined with the aqueous phase and extracted by the ethyl acetate two additional times. The organic layers were dried over Mg_2SO_4 and concentrated to give 168.2 mg (0.87 mmol, 87%) product as a brown liquid. Spectroscopic data is consistent with reported values.¹⁰ ^1H NMR (300 MHz, CDCl_3): δ 7.92 (m, 2H), 6.91 (m, 2H), 4.02 (t, J = 6.5 Hz, 2H), 2.55 (s, 3H), 1.78 (m, 2H), 1.50 (m, 2H), 0.98 (t, J = 7.03 Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 196.8, 163.1, 130.5, 130.0, 114.1, 67.9, 31.1, 26.3, 19.2, 13.8.

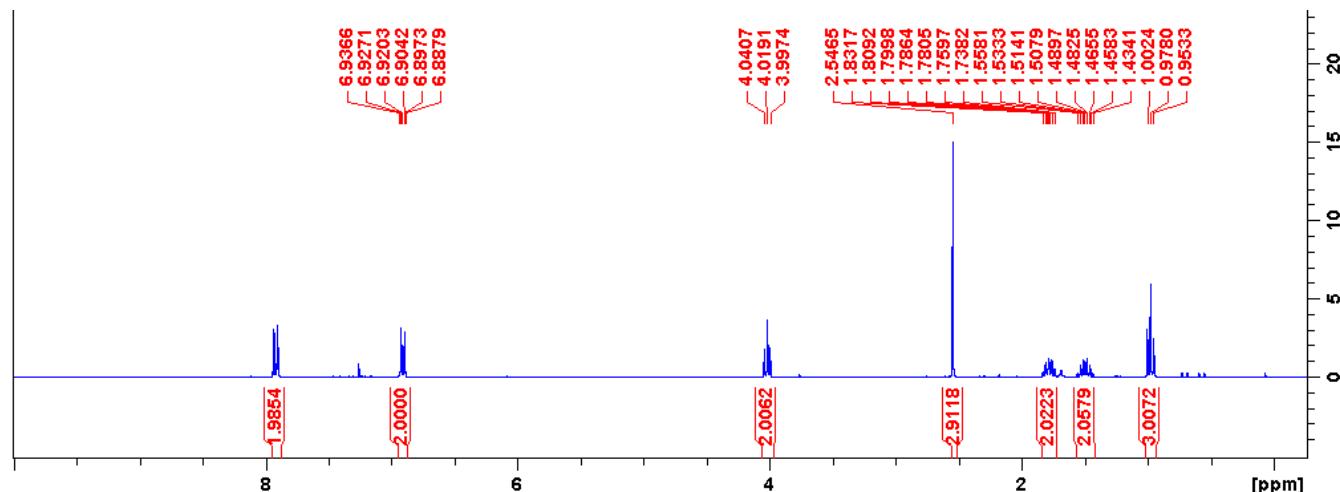
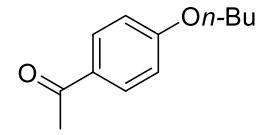


Figure S118. ^1H NMR spectrum (300 MHz; CDCl_3) of 1-(4-n-Butoxyphenyl)ethanone

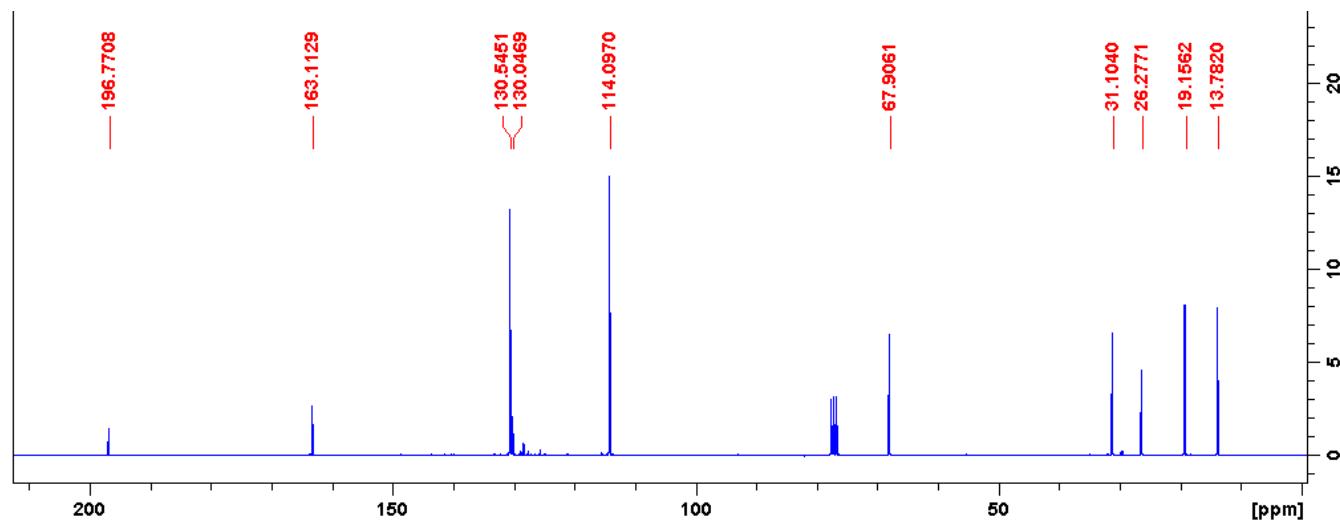


Figure S119. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (75 MHz; CDCl_3) of 1-(4-n-Butoxyphenyl)ethanone

2,2',7,7'-Tetrakis-di(*p*-methoxyphenylamino)-9,9'-spirobifluorene (*spiro*-OMeTAD)

A 4-dram vial was charged with 2,2',7,7'-tetrabromo-9,9'-spirobifluorene (632 mg, 1.00 mmol), 4,4'-dimethoxydiphenylamine (940 mg, 4.10 mmol), NaOtBu (480.5 mg, 5.00 mmol), **6** (6.2 mg, 0.01 mmol), and 10 mL of THF. The mixture was stirred at 80 °C for 24 h. The solvent was evaporated *in vacuo*. The residue was dissolved in minimal toluene, and passed through a silica plug (toluene:TBME, 20:1 eluent). The resulting solution was concentrated to give an orange solid. The solid was dissolved in 5 mL of THF, followed by the addition of 30 mL of methanol (anti-solvent) to crystallize the product. Pale yellow solid: 994.4 mg (0.81 mmol, 81% yield). Spectroscopic data is consistent with reported values.¹¹ ¹H NMR (500 MHz, *d*⁶-DMSO): δ 3.72 (s, 24 H, 8 x –OCH₃), 6.19 (d, 4H, *J* = 2.0 Hz), 6.70 (dd, 4H, *J* = 2.0, 8.4 Hz), 6.84 (m, 32H, Ar–H), 7.48 (d, 4H, *J* = 8.4 Hz). ¹³C NMR (125 MHz, *d*⁶-DMSO): δ 155.7, 149.9, 147.7, 140.9, 134.4, 126.0, 121.4, 120.7, 116.2, 116.1, 65.4, 55.7. NOTE: Initial purification attempts using standard flash column chromatography (hexanes/ethyl acetate eluent; material loaded as a DCM solution) resulted in low recovered yields due to suspected decomposition of the product (formation of multiple new colored species).

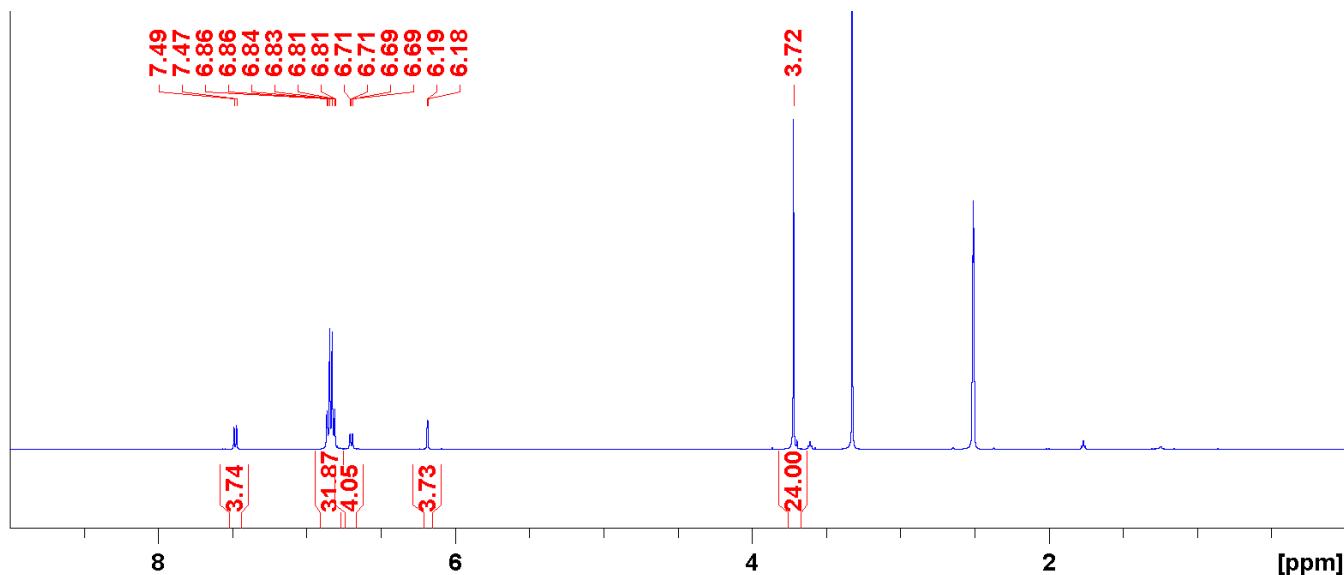
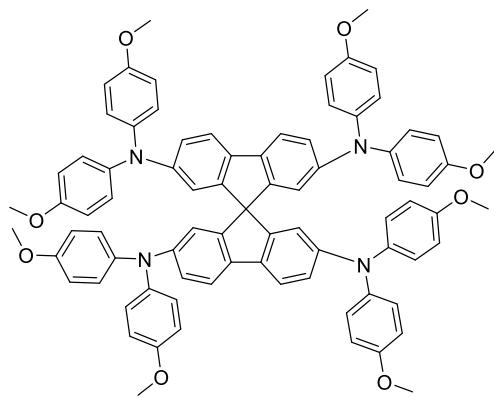


Figure S120. ¹H NMR spectrum (500 MHz; *d*⁶-DMSO) of Spiro-OMeTAD

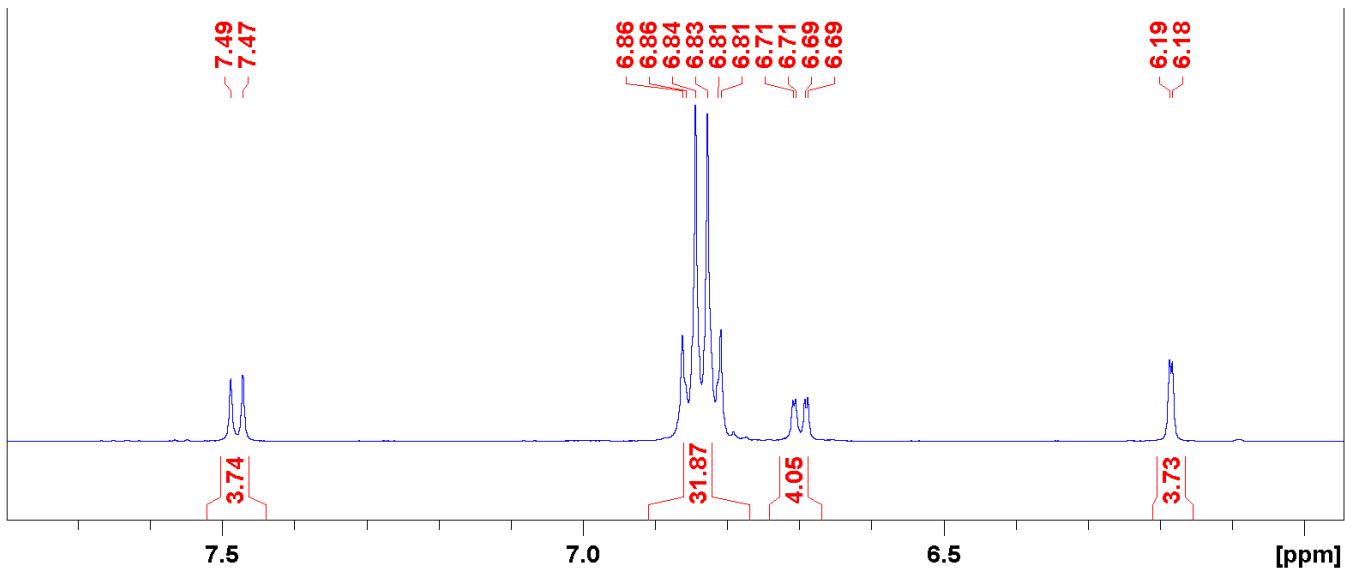


Figure S121. ^1H NMR spectrum (500 MHz; d^6 -DMSO) of spiro-OMeTAD. Expansion of aromatic region.

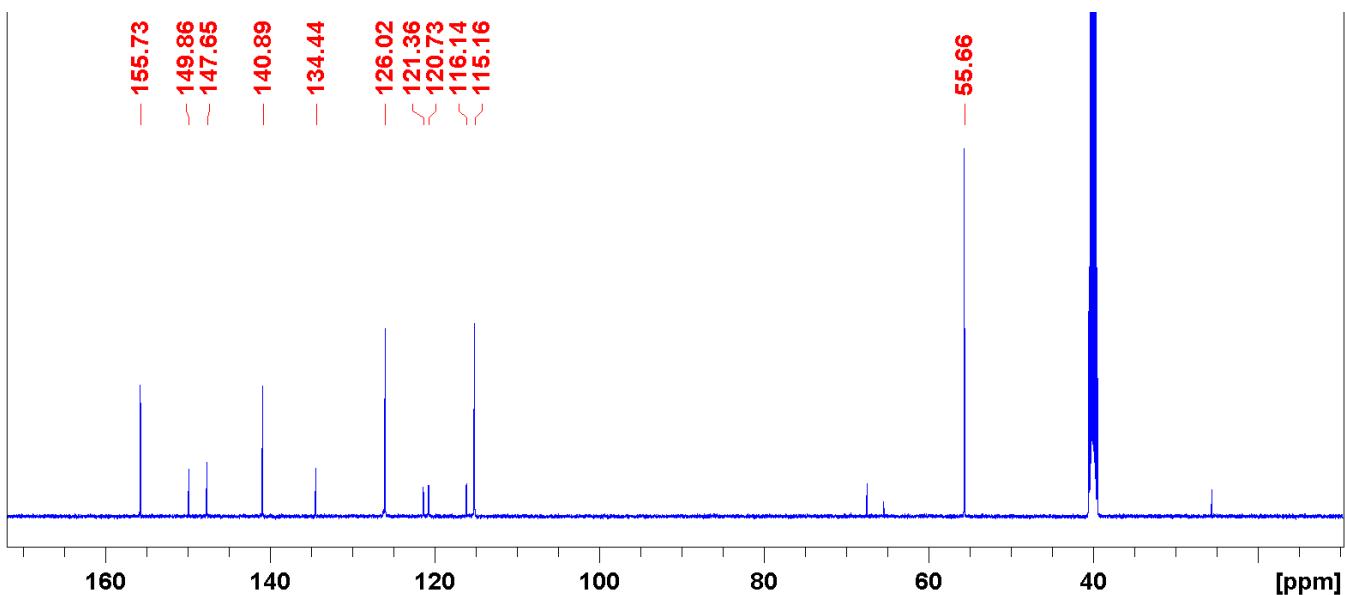


Figure S122. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (125 MHz; d^6 -DMSO) of spiro-OMeTAD. Signals at 26.0 and 67.5 ppm are trace residual THF from the recrystallization.

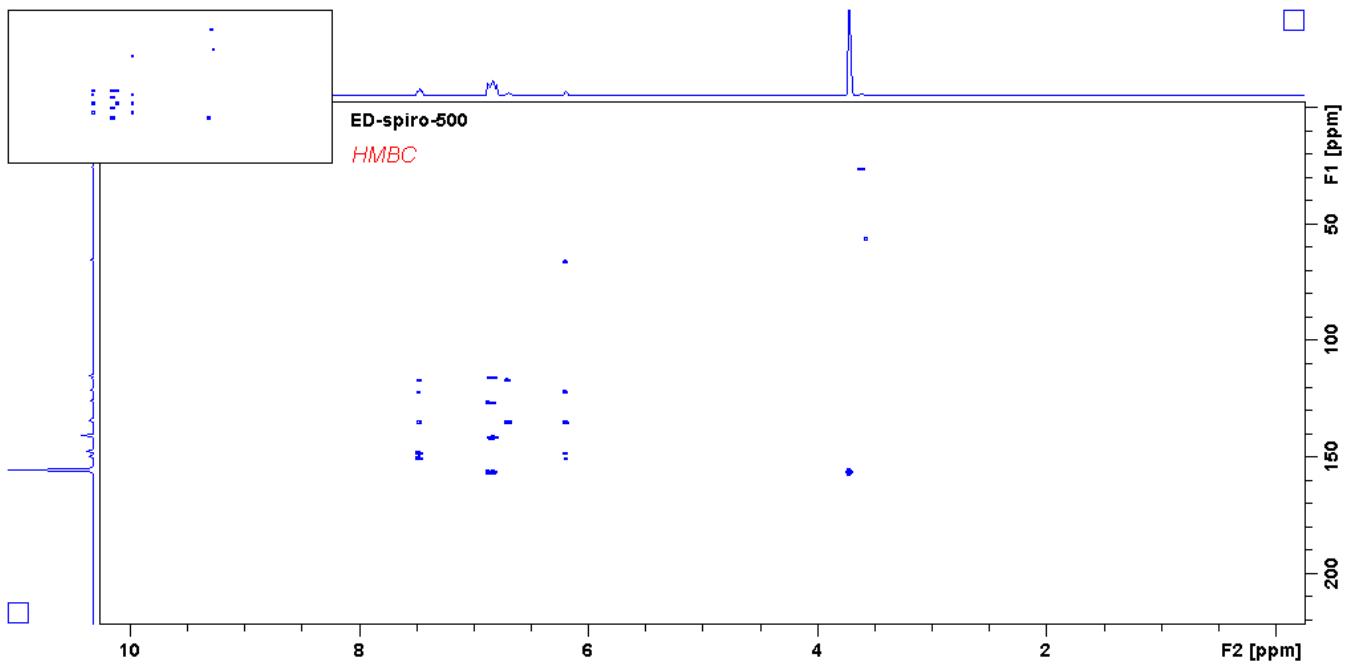


Figure S123. ^1H - ^{13}C HMBC NMR spectrum (500 MHz and 125 MHz; d^6 -DMSO) of *spiro*-OMeTAD.

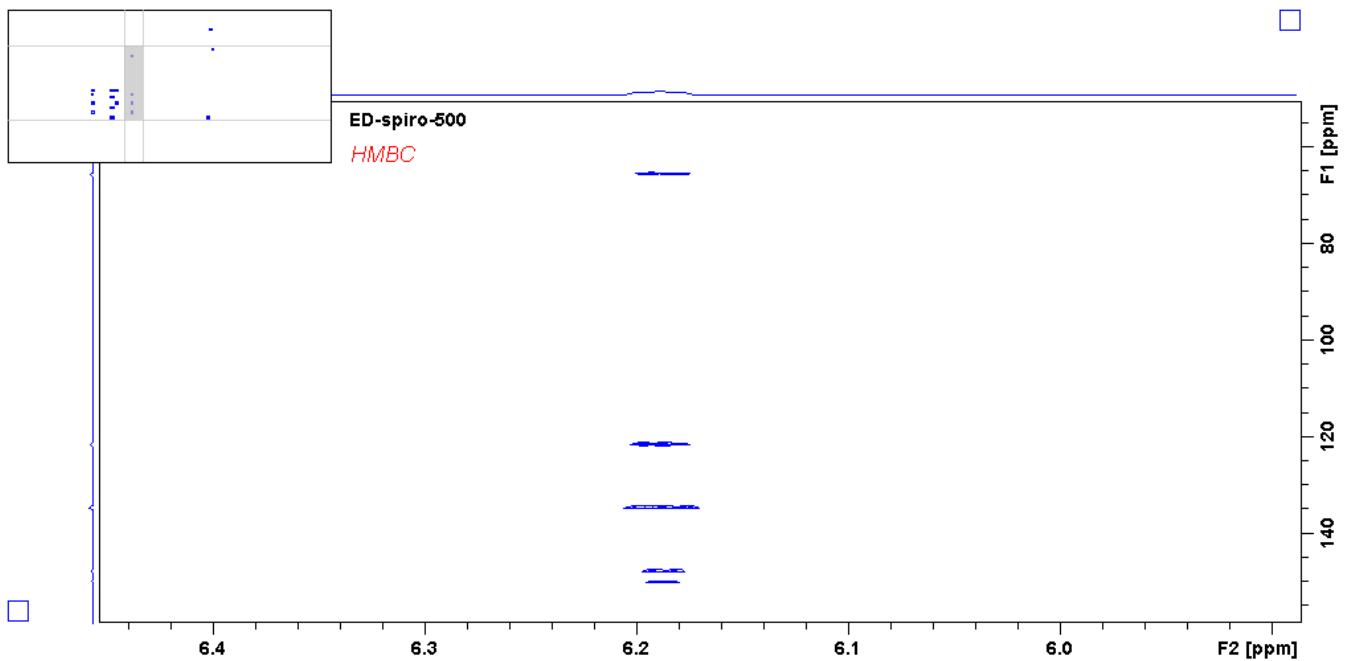


Figure S124. Expansion of ^1H - ^{13}C HMBC NMR spectrum (500 MHz and 125 MHz; d^6 -DMSO) of *spiro*-OMeTAD.
Signal at 65.4 is confirmed as the central *spiro*-carbon (quaternary).

V: X-ray Crystallographic Details

^{DMP}DAB–Pd–MAH (**1**)

Single crystals of $C_{22}H_{22}N_2O_3Pd$ (**1**) were selected using a MitEGen loop using paratone oil. A suitable crystal was selected and run Bruker APEX-II CCD diffractometer. The crystal was kept at 99.96 K during data collection. Using Olex2,¹² the structure was solved with the olex2.solve¹³ structure solution program using Charge Flipping and refined with the XL¹⁴ refinement package using Least Squares minimization.

Crystal structure determination of [1]

Crystal Data for $C_{22}H_{22}N_2O_3Pd$ ($M = 468.81$ g/mol): triclinic, space group P-1 (no. 2), $a = 9.1137(9)$ Å, $b = 10.2220(10)$ Å, $c = 12.2985(12)$ Å, $\alpha = 70.989(2)^\circ$, $\beta = 70.567(2)^\circ$, $\gamma = 71.163(2)^\circ$, $V = 991.53(17)$ Å³, $Z = 2$, $T = 99.96$ K, $\mu(\text{MoK}\alpha) = 0.961$ mm⁻¹, $D_{\text{calc}} = 1.570$ g/cm³, 16832 reflections measured ($3.622^\circ \leq 2\Theta \leq 56.148^\circ$), 4746 unique ($R_{\text{int}} = 0.0136$, $R_{\text{sigma}} = 0.0130$) which were used in all calculations. The final R_1 was 0.0162 ($I > 2\sigma(I)$) and wR_2 was 0.0427 (all data).

Table S17 Crystal data and structure refinement for **1**.

Identification code	1
Empirical formula	$C_{22}H_{22}N_2O_3Pd$
Formula weight	468.81
Temperature/K	99.96
Crystal system	triclinic
Space group	P-1
$a/\text{\AA}$	9.1137(9)
$b/\text{\AA}$	10.2220(10)
$c/\text{\AA}$	12.2985(12)
$\alpha/^\circ$	70.989(2)
$\beta/^\circ$	70.567(2)
$\gamma/^\circ$	71.163(2)
Volume/Å ³	991.53(17)
Z	2
$\rho_{\text{calc}}/\text{g/cm}^3$	1.570
μ/mm^{-1}	0.961
$F(000)$	476.0
Crystal size/mm ³	0.75 × 0.75 × 0.1
Radiation	MoK α ($\lambda = 0.71073$)
2 Θ range for data collection/°	3.622 to 56.148
Index ranges	-12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -16 ≤ l ≤ 16
Reflections collected	16832
Independent reflections	4746 [$R_{\text{int}} = 0.0136$, $R_{\text{sigma}} = 0.0130$]
Data/restraints/parameters	4746/0/257
Goodness-of-fit on F^2	1.063
Final R indexes [$I >= 2\sigma(I)$]	$R_1 = 0.0162$, $wR_2 = 0.0422$
Final R indexes [all data]	$R_1 = 0.0171$, $wR_2 = 0.0427$
Largest diff. peak/hole / e Å ⁻³	0.48/-0.36

Table S18 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 1. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U(eq)
Pd1	5717.1(2)	6331.2(2)	8038.0(2)	10.41(3)
O2	2223.7(12)	7193.9(11)	7649.9(9)	18.8(2)
O3	1919.2(14)	9109.9(12)	8301.7(12)	29.2(3)
O1	2650.9(13)	4936.4(12)	7550.2(10)	23.0(2)
N2	7962.5(13)	5292.7(12)	7024.3(10)	12.3(2)
N1	7259.4(13)	7690.4(12)	7683.7(10)	12.4(2)
C22	2488.9(16)	7861.3(15)	8381.6(13)	18.5(3)
C20	3733.6(16)	5449.0(14)	8887.5(12)	13.8(2)
C2	9120.6(16)	5838.7(15)	6863.0(13)	16.7(3)
C1	8735.4(16)	7158.6(15)	7244.3(12)	15.8(3)
C4	9295.4(16)	2784.8(15)	6988.9(12)	15.4(3)
C5	9533.9(17)	1647.3(15)	6506.0(13)	18.3(3)
C6	8782.9(17)	1801.7(15)	5647.2(13)	18.6(3)
C9	6522.3(18)	5703.9(15)	5207.6(13)	19.0(3)
C8	7521.7(16)	4264.7(14)	5687.4(12)	14.3(2)
C14	5800.8(17)	10163.3(15)	7429.5(13)	17.0(3)
C19	3464.8(16)	6786.8(14)	9147.6(12)	15.2(2)
C12	7320.3(16)	9082.5(15)	8955.0(12)	16.2(3)
C18	5317(2)	10058.3(16)	6409.4(14)	23.7(3)
C15	5334.3(18)	11443.0(15)	7765.8(14)	21.8(3)
C3	8288.6(15)	4080.0(14)	6562.3(12)	12.8(2)
C7	7780.7(17)	3099.5(15)	5241.7(12)	17.2(3)
C17	6827.7(18)	10389.7(16)	9253.9(13)	21.3(3)
C13	6806.9(16)	9005.0(14)	8028.8(12)	13.6(2)
C21	2877.6(16)	5714.7(15)	7990.6(12)	15.4(3)
C10	10068.2(18)	2576.2(16)	7963.0(14)	21.0(3)
C11	8295.0(18)	7816.8(16)	9668.5(13)	20.2(3)
C16	5857.2(19)	11550.1(16)	8662.9(15)	24.3(3)

Table S19 Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 1. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^*{}^2U_{11} + 2hka^*b^*U_{12} + \dots]$.

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Pd1	9.34(5)	9.60(5)	13.25(5)	-3.94(4)	-3.31(3)	-1.93(3)
O2	16.7(5)	17.6(5)	23.1(5)	-3.0(4)	-10.1(4)	-2.2(4)
O3	22.2(6)	15.5(5)	47.4(7)	-10.0(5)	-11.3(5)	3.4(4)
O1	27.0(6)	25.9(5)	23.9(5)	-8.4(4)	-8.1(4)	-12.7(5)
N2	13.0(5)	11.1(5)	12.8(5)	-3.7(4)	-3.9(4)	-1.3(4)
N1	14.8(5)	10.9(5)	13.2(5)	-3.1(4)	-4.6(4)	-4.1(4)
C22	11.8(6)	18.1(6)	25.1(7)	-7.0(6)	-3.0(5)	-2.9(5)
C20	13.1(6)	14.2(6)	14.5(6)	-3.1(5)	-3.3(5)	-4.6(5)
C2	13.3(6)	16.1(6)	20.6(6)	-7.3(5)	-1.5(5)	-3.6(5)
C1	14.4(6)	16.7(6)	19.2(6)	-6.2(5)	-3.4(5)	-6.5(5)
C4	13.8(6)	14.9(6)	16.8(6)	-4.5(5)	-3.6(5)	-2.1(5)
C5	17.7(7)	12.2(6)	22.8(7)	-5.1(5)	-3.9(5)	-1.0(5)
C6	20.7(7)	14.9(6)	20.8(7)	-8.6(5)	-1.2(5)	-4.9(5)
C9	23.1(7)	15.7(6)	18.8(7)	-4.0(5)	-9.8(6)	-1.1(5)
C8	14.6(6)	14.3(6)	13.3(6)	-2.9(5)	-2.3(5)	-4.2(5)
C14	17.3(6)	14.2(6)	18.6(6)	-2.7(5)	-3.3(5)	-5.2(5)
C19	12.2(6)	16.5(6)	17.7(6)	-7.0(5)	-2.2(5)	-3.3(5)
C12	16.0(6)	19.4(6)	15.5(6)	-5.9(5)	-0.7(5)	-8.8(5)
C18	28.0(8)	19.6(7)	24.8(7)	-0.7(6)	-14.0(6)	-4.5(6)
C15	20.9(7)	13.0(6)	26.5(7)	-3.2(6)	-2.0(6)	-3.1(5)
C3	12.3(6)	12.0(6)	13.7(6)	-4.2(5)	-1.0(5)	-3.7(5)
C7	19.4(7)	18.6(6)	15.8(6)	-5.6(5)	-4.0(5)	-6.5(5)
C17	23.3(7)	24.0(7)	20.8(7)	-11.6(6)	0.7(6)	-11.5(6)
C13	13.9(6)	12.0(6)	15.9(6)	-4.8(5)	-1.0(5)	-5.8(5)
C21	12.7(6)	16.8(6)	16.0(6)	-2.8(5)	-2.2(5)	-5.4(5)
C10	21.9(7)	18.1(7)	24.5(7)	-6.0(6)	-12.5(6)	1.0(5)
C11	20.1(7)	25.5(7)	18.1(7)	-6.1(6)	-6.4(5)	-7.3(6)
C16	26.3(8)	17.1(7)	29.3(8)	-12.9(6)	3.1(6)	-8.0(6)

Table S20 Bond Lengths for 1.

Atom	Atom	Length/ \AA	Atom	Atom	Length/ \AA
Pd1	N2	2.1520(11)	C4	C5	1.3974(19)
Pd1	N1	2.1342(11)	C4	C3	1.3976(18)
Pd1	C20	2.0868(13)	C4	C10	1.5082(19)
Pd1	C19	2.0556(14)	C5	C6	1.383(2)
O2	C22	1.4089(18)	C6	C7	1.390(2)
O2	C21	1.4101(17)	C9	C8	1.5063(18)
O3	C22	1.1968(18)	C8	C3	1.4016(18)
O1	C21	1.1959(17)	C8	C7	1.3902(19)
N2	C2	1.2782(18)	C14	C18	1.506(2)
N2	C3	1.4341(16)	C14	C15	1.393(2)
N1	C1	1.2777(18)	C14	C13	1.4021(19)
N1	C13	1.4329(16)	C12	C17	1.395(2)
C22	C19	1.4620(19)	C12	C13	1.4001(19)
C20	C19	1.4315(18)	C12	C11	1.507(2)
C20	C21	1.4628(18)	C15	C16	1.385(2)
C2	C1	1.4697(19)	C17	C16	1.381(2)

Table S21 Bond Angles for 1.

Atom	Atom	Atom	Angle/ $^{\circ}$	Atom	Atom	Atom	Angle/ $^{\circ}$
N1	Pd1	N2	76.30(4)	C3	C8	C9	120.55(12)
C20	Pd1	N2	124.67(5)	C7	C8	C9	121.54(12)
C20	Pd1	N1	157.61(5)	C7	C8	C3	117.84(12)
C19	Pd1	N2	164.64(5)	C15	C14	C18	120.86(13)
C19	Pd1	N1	117.93(5)	C15	C14	C13	117.70(13)
C19	Pd1	C20	40.42(5)	C13	C14	C18	121.34(13)
C22	O2	C21	108.65(11)	C22	C19	Pd1	104.94(9)
C2	N2	Pd1	113.36(9)	C20	C19	Pd1	70.96(8)
C2	N2	C3	118.58(11)	C20	C19	C22	107.11(12)
C3	N2	Pd1	128.03(8)	C17	C12	C13	117.36(13)
C1	N1	Pd1	114.08(9)	C17	C12	C11	119.35(13)
C1	N1	C13	119.67(11)	C13	C12	C11	123.22(13)
C13	N1	Pd1	125.75(9)	C16	C15	C14	120.45(14)
O2	C22	C19	108.48(11)	C4	C3	N2	121.02(12)
O3	C22	O2	119.52(14)	C4	C3	C8	122.60(12)
O3	C22	C19	131.99(15)	C8	C3	N2	116.37(11)
C19	C20	Pd1	68.61(7)	C6	C7	C8	120.67(13)
C19	C20	C21	107.01(11)	C16	C17	C12	120.85(14)
C21	C20	Pd1	106.96(9)	C14	C13	N1	117.05(12)
N2	C2	C1	117.65(12)	C12	C13	N1	120.19(12)
N1	C1	C2	117.22(12)	C12	C13	C14	122.73(12)
C5	C4	C3	117.57(13)	O2	C21	C20	108.41(11)
C5	C4	C10	120.03(12)	O1	C21	O2	119.20(13)
C3	C4	C10	122.37(12)	O1	C21	C20	132.38(13)
C6	C5	C4	120.87(13)	C17	C16	C15	120.89(13)
C5	C6	C7	120.45(13)				

Table S22 Hydrogen Atom Coordinates ($\text{\AA} \times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 1.

Atom	x	y	z	U(eq)
H20	3801	4543	9526	17
H2	10193	5407	6509	20
H1	9550	7598	7167	19
H5	10221	756	6771	22
H6	8953	1016	5332	22
H9A	5625	6006	5854	28
H9B	6107	5643	4591	28
H9C	7185	6399	4866	28
H19	3317	6844	9975	18
H18A	4469	10899	6201	36
H18B	4920	9197	6642	36
H18C	6247	10010	5721	36
H15	4653	12248	7377	26
H7	7268	3191	4654	21
H17	7164	10483	9872	26
H10A	10337	1560	8356	32
H10B	9322	3106	8546	32
H10C	11047	2927	7620	32
H11A	9423	7859	9386	30
H11B	8196	6936	9573	30
H11C	7900	7832	10510	30
H16	5544	12434	8874	29

Refinement model description

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

Details:

1. Fixed Uiso

At 1.2 times of:

All C(H) groups

At 1.5 times of:

All C(H,H,H) groups

2.a Ternary CH refined with riding coordinates:

C20(H20), C19(H19)

2.b Aromatic/amide H refined with riding coordinates:

C2(H2), C1(H1), C5(H5), C6(H6), C15(H15), C7(H7), C17(H17), C16(H16)

2.c Idealised Me refined as rotating group:

C9(H9A,H9B,H9C), C18(H18A,H18B,H18C), C10(H10A,H10B,H10C), C11(H11A,H11B,H11C)

DPEPhos–Pd–MAH (3)

Single crystals of $C_{44}H_{40}O_5P_2Pd$ [**3•Et₂O**] were selected using a MiteEGen loop using paratone oil. A suitable crystal was selected run on a Bruker APEX-II CCD diffractometer. The crystal was kept at 273.15 K during data collection. Using Olex2,¹² the structure was solved with the olex2.solve¹³ structure solution program using Charge Flipping and refined with the XL¹⁴ refinement package using Least Squares minimization.

Crystal structure determination of [3]

Crystal Data for $C_{44}H_{40}O_5P_2Pd$ ($M = 817.10$ g/mol): triclinic, space group P-1 (no. 2), $a = 11.0488(7)$ Å, $b = 12.4133(8)$ Å, $c = 15.6581(10)$ Å, $\alpha = 99.623(2)^\circ$, $\beta = 106.450(2)^\circ$, $\gamma = 105.981(2)^\circ$, $V = 1908.8(2)$ Å³, $Z = 2$, $T = 273.15$ K, $\mu(\text{MoK}\alpha) = 0.615$ mm⁻¹, $D_{\text{calc}} = 1.422$ g/cm³, 75385 reflections measured ($5.074^\circ \leq 2\Theta \leq 56.036^\circ$), 9217 unique ($R_{\text{int}} = 0.0824$, $R_{\text{sigma}} = 0.0586$) which were used in all calculations. The final R_1 was 0.0541 ($I > 2\sigma(I)$) and wR_2 was 0.1133 (all data).

Table S23 Crystal data and structure refinement for 3.

Identification code	3
Empirical formula	$C_{44}H_{40}O_5P_2Pd$
Formula weight	817.10
Temperature/K	273.15
Crystal system	triclinic
Space group	P-1
$a/\text{\AA}$	11.0488(7)
$b/\text{\AA}$	12.4133(8)
$c/\text{\AA}$	15.6581(10)
$\alpha/^\circ$	99.623(2)
$\beta/^\circ$	106.450(2)
$\gamma/^\circ$	105.981(2)
Volume/Å ³	1908.8(2)
Z	2
$\rho_{\text{calc}}/\text{g/cm}^3$	1.422
μ/mm^{-1}	0.615
F(000)	840.0
Crystal size/mm ³	0.15 × 0.15 × 0.12
Radiation	MoKα ($\lambda = 0.71073$)
2θ range for data collection/°	5.074 to 56.036
Index ranges	-14 ≤ h ≤ 14, -16 ≤ k ≤ 16, -20 ≤ l ≤ 20
Reflections collected	75385
Independent reflections	9217 [$R_{\text{int}} = 0.0824$, $R_{\text{sigma}} = 0.0586$]
Data/restraints/parameters	9217/0/471
Goodness-of-fit on F^2	1.065
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0541$, $wR_2 = 0.0983$
Final R indexes [all data]	$R_1 = 0.0931$, $wR_2 = 0.1133$
Largest diff. peak/hole / e Å ⁻³	1.18/-0.63

Table S24 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 3. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	$U(\text{eq})$
Pd1	1950.7(3)	2579.2(3)	6130.4(2)	30.46(9)
P1	3063.1(9)	1378.1(8)	5689.8(7)	29.6(2)
P2	3131.2(9)	3511.8(8)	7683.7(7)	32.5(2)
O1	3072(2)	1144(2)	7613.7(17)	36.4(6)
O3	1661(4)	4477(3)	5077(3)	70.4(10)
C17	3081(3)	121(3)	6162(3)	32.6(8)
O4	1110(4)	5314(3)	6224(3)	90.8(13)
C22	3006(4)	126(3)	7034(3)	36.9(9)
C5	2432(4)	687(3)	4450(3)	35.2(8)
C29	3960(4)	5066(3)	7878(3)	40.9(9)
C40	2139(4)	3455(3)	8443(3)	37.0(9)
O2	1702(5)	3189(4)	3910(3)	92.8(13)
C11	4809(4)	2229(3)	5934(3)	35.9(9)
C18	3073(4)	-908(3)	5638(3)	40.9(9)
C1	498(4)	2548(3)	4911(3)	39.7(9)
C2	366(4)	3232(3)	5660(3)	41.7(10)
C12	5883(4)	1956(4)	6422(3)	46.1(10)
C28	4524(4)	3080(3)	8280(3)	36.7(9)
C23	4350(4)	1909(3)	8143(3)	36.1(9)
C30	4019(5)	5899(4)	8606(3)	57.8(12)
C10	1084(4)	12(4)	4035(3)	45.7(10)
C19	2936(4)	-1890(4)	5957(3)	48.7(11)
C21	2838(4)	-861(4)	7349(3)	49.8(11)
C24	5382(4)	1532(4)	8543(3)	51.6(11)
C20	2794(4)	-1872(4)	6795(3)	52.9(12)
C35	1030(4)	3800(4)	8212(3)	55.5(12)
C16	5059(4)	3243(4)	5654(4)	53.5(12)
C27	5791(4)	3876(4)	8835(3)	48.2(11)
C3	1032(5)	4437(4)	5733(4)	58.2(13)
C6	3222(5)	808(4)	3901(3)	49.1(11)
C39	2437(5)	3086(4)	9227(3)	56.8(12)
C4	1310(5)	3343(5)	4537(3)	56.6(12)
C13	7186(4)	2701(5)	6624(4)	65.0(14)
C9	537(5)	-527(4)	3109(3)	59.6(13)
C8	1323(6)	-397(5)	2574(4)	68.3(15)
C26	6827(4)	3501(5)	9234(3)	61.2(13)
C15	6348(5)	3970(4)	5859(4)	69.9(16)
C36	237(5)	3764(5)	8753(4)	68.0(15)
C25	6622(5)	2339(5)	9088(3)	63.5(14)
C7	2662(6)	270(5)	2965(3)	66.0(14)
C34	4600(6)	5426(5)	7287(4)	70.4(15)
C31	4730(6)	7054(5)	8741(4)	79.4(17)
C38	1639(6)	3054(5)	9765(4)	78.1(17)
C37	538(5)	3386(5)	9522(4)	71.7(16)
C14	7403(5)	3695(5)	6344(4)	73.4(17)
C32	5387(7)	7394(5)	8167(5)	86.1(19)
C33	5324(7)	6584(6)	7436(5)	91(2)
O5	1078(9)	-1553(9)	9039(5)	193(3)
C43	973(12)	-590(9)	9222(6)	139(4)
C42	-3(12)	-2374(13)	8235(6)	208(6)
C44	2260(20)	150(12)	10034(12)	397(17)
C41	599(12)	-3198(8)	8258(6)	145(5)

Table S25 Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 3. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^*{}^2U_{11} + 2hka^*b^*U_{12} + \dots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pd1	24.03(14)	31.88(16)	34.36(16)	8.98(12)	8.04(11)	9.92(11)
P1	23.8(4)	30.4(5)	34.7(5)	8.5(4)	11.2(4)	8.2(4)
P2	28.1(5)	33.2(5)	33.3(5)	5.2(4)	7.6(4)	11.2(4)
O1	33.0(14)	34.9(14)	36.4(15)	6.2(12)	7.0(11)	11.0(11)
O3	69(2)	52(2)	83(3)	39(2)	15(2)	9.9(18)
C17	24.7(17)	29.2(19)	42(2)	9.7(17)	9.7(16)	7.8(15)
O4	94(3)	43(2)	113(3)	3(2)	5(3)	33(2)
C22	31.4(19)	32(2)	41(2)	7.5(17)	5.9(17)	9.1(16)
C5	36(2)	34(2)	40(2)	13.2(17)	14.7(17)	14.6(17)
C29	37(2)	39(2)	42(2)	12.0(19)	6.6(18)	13.7(18)
C40	31.8(19)	34(2)	38(2)	1.0(17)	10.0(17)	7.6(16)
O2	108(3)	120(4)	65(3)	48(3)	42(3)	34(3)
C11	27.1(18)	33(2)	45(2)	4.1(17)	16.3(17)	6.4(16)
C18	34(2)	38(2)	50(3)	6.7(19)	13.7(18)	16.5(18)
C1	25.5(18)	38(2)	45(2)	11.1(19)	-0.9(17)	8.7(16)
C2	29.9(19)	41(2)	53(3)	14(2)	7.8(18)	15.6(18)
C12	32(2)	49(3)	53(3)	4(2)	14.6(19)	11.8(19)
C28	29.4(19)	45(2)	35(2)	7.5(18)	9.4(16)	15.9(17)
C23	31.0(19)	43(2)	31(2)	7.5(17)	5.9(16)	13.3(17)
C30	65(3)	44(3)	58(3)	9(2)	17(2)	16(2)
C10	41(2)	45(2)	47(3)	7(2)	17(2)	10.7(19)
C19	41(2)	32(2)	62(3)	4(2)	3(2)	17.5(19)
C21	53(3)	43(3)	49(3)	19(2)	12(2)	13(2)
C24	48(3)	49(3)	50(3)	7(2)	3(2)	23(2)
C20	52(3)	32(2)	64(3)	18(2)	5(2)	11(2)
C35	43(2)	83(4)	44(3)	12(2)	14(2)	30(2)
C16	44(2)	43(3)	83(4)	21(2)	35(2)	14(2)
C27	34(2)	46(3)	48(3)	-3(2)	-0.6(19)	11.9(19)
C3	51(3)	44(3)	70(3)	17(3)	-1(2)	24(2)
C6	49(3)	52(3)	51(3)	15(2)	24(2)	16(2)
C39	58(3)	73(3)	58(3)	29(3)	31(2)	34(3)
C4	52(3)	70(4)	47(3)	28(3)	8(2)	21(3)
C13	28(2)	81(4)	67(3)	1(3)	8(2)	10(2)
C9	55(3)	51(3)	51(3)	1(2)	5(2)	7(2)
C8	89(4)	58(3)	41(3)	5(2)	8(3)	20(3)
C26	34(2)	68(3)	59(3)	-3(3)	-4(2)	15(2)
C15	59(3)	43(3)	116(5)	20(3)	55(3)	5(2)
C36	39(3)	99(4)	58(3)	-1(3)	15(2)	27(3)
C25	44(3)	73(4)	60(3)	5(3)	-4(2)	31(3)
C7	94(4)	69(3)	49(3)	18(3)	41(3)	31(3)
C34	79(4)	58(3)	68(4)	12(3)	36(3)	7(3)
C31	94(4)	40(3)	82(4)	7(3)	9(4)	16(3)
C38	87(4)	103(5)	71(4)	43(3)	48(3)	41(4)
C37	54(3)	93(4)	64(4)	8(3)	36(3)	12(3)
C14	38(3)	59(3)	103(4)	-11(3)	36(3)	-7(2)
C32	94(5)	44(3)	101(5)	31(4)	10(4)	10(3)
C33	93(5)	74(4)	99(5)	43(4)	39(4)	-2(4)
O5	211(8)	215(9)	102(5)	60(6)	11(5)	27(7)
C43	237(12)	129(8)	84(6)	24(5)	40(6)	134(9)
C42	184(11)	306(18)	55(5)	24(8)	9(6)	12(12)
C44	590(40)	136(12)	242(18)	8(12)	-100(20)	67(17)
C41	287(14)	138(8)	135(8)	90(7)	151(9)	150(9)

Table S26 Bond Lengths for 3.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pd1	P1	2.3140(10)	C2	C3	1.443(6)
Pd1	P2	2.3211(10)	C12	C13	1.393(6)
Pd1	C1	2.104(4)	C28	C23	1.383(5)
Pd1	C2	2.125(4)	C28	C27	1.398(5)
P1	C17	1.837(4)	C23	C24	1.378(5)
P1	C5	1.827(4)	C30	C31	1.379(7)
P1	C11	1.819(4)	C10	C9	1.368(6)
P2	C29	1.824(4)	C19	C20	1.363(6)
P2	C40	1.829(4)	C21	C20	1.381(6)
P2	C28	1.827(4)	C24	C25	1.380(6)
O1	C22	1.398(5)	C35	C36	1.378(6)
O1	C23	1.385(4)	C16	C15	1.371(6)
O3	C3	1.393(6)	C27	C26	1.380(6)
O3	C4	1.401(6)	C6	C7	1.381(6)
C17	C22	1.390(5)	C39	C38	1.379(7)
C17	C18	1.394(5)	C13	C14	1.360(8)
O4	C3	1.190(6)	C9	C8	1.364(7)
C22	C21	1.382(6)	C8	C7	1.375(7)
C5	C10	1.387(5)	C26	C25	1.366(7)
C5	C6	1.386(5)	C15	C14	1.362(8)
C29	C30	1.378(6)	C36	C37	1.353(7)
C29	C34	1.376(6)	C34	C33	1.382(7)
C40	C35	1.381(6)	C31	C32	1.357(9)
C40	C39	1.366(6)	C38	C37	1.364(8)
O2	C4	1.188(6)	C32	C33	1.363(9)
C11	C12	1.379(5)	O5	C43	1.227(10)
C11	C16	1.383(6)	O5	C42	1.449(12)
C18	C19	1.379(6)	C43	C44	1.534(17)
C1	C2	1.396(6)	C42	C41	1.365(15)
C1	C4	1.458(6)			

Table S27 Bond Angles for 3.

Atom	Atom	Atom	Angle/ [°]	Atom	Atom	Atom	Angle/ [°]
P1	Pd1	P2	106.32(3)	C3	C2	Pd1	104.7(3)
C1	Pd1	P1	106.38(12)	C11	C12	C13	119.7(4)
C1	Pd1	P2	146.24(12)	C23	C28	P2	118.9(3)
C1	Pd1	C2	38.55(15)	C23	C28	C27	117.8(3)
C2	Pd1	P1	144.86(12)	C27	C28	P2	123.2(3)
C2	Pd1	P2	108.67(12)	C28	C23	O1	116.2(3)
C17	P1	Pd1	120.04(12)	C24	C23	O1	122.2(4)
C5	P1	Pd1	114.03(12)	C24	C23	C28	121.5(4)
C5	P1	C17	101.12(17)	C29	C30	C31	120.3(5)
C11	P1	Pd1	109.82(12)	C9	C10	C5	121.5(4)
C11	P1	C17	106.39(17)	C20	C19	C18	120.2(4)
C11	P1	C5	103.95(17)	C20	C21	C22	119.0(4)
C29	P2	Pd1	112.16(14)	C23	C24	C25	119.4(4)
C29	P2	C40	103.35(18)	C19	C20	C21	120.5(4)
C29	P2	C28	101.66(18)	C36	C35	C40	120.9(5)
C40	P2	Pd1	116.15(13)	C15	C16	C11	121.0(5)
C28	P2	Pd1	118.03(13)	C26	C27	C28	120.8(4)
C28	P2	C40	103.53(18)	O3	C3	C2	108.0(4)
C23	O1	C22	115.8(3)	O4	C3	O3	120.1(5)
C3	O3	C4	108.6(4)	O4	C3	C2	131.9(6)
C22	C17	P1	121.3(3)	C7	C6	C5	120.0(4)
C22	C17	C18	117.0(4)	C40	C39	C38	120.5(5)
C18	C17	P1	121.6(3)	O3	C4	C1	108.2(4)
C17	C22	O1	120.1(3)	O2	C4	O3	119.4(5)
C21	C22	O1	118.0(4)	O2	C4	C1	132.4(5)
C21	C22	C17	121.9(4)	C14	C13	C12	120.4(5)
C10	C5	P1	118.1(3)	C8	C9	C10	119.8(5)
C6	C5	P1	123.6(3)	C9	C8	C7	120.1(5)
C6	C5	C10	118.2(4)	C25	C26	C27	120.0(4)
C30	C29	P2	123.4(3)	C14	C15	C16	119.9(5)
C34	C29	P2	118.4(4)	C37	C36	C35	120.1(5)
C34	C29	C30	118.1(4)	C26	C25	C24	120.4(4)
C35	C40	P2	118.3(3)	C8	C7	C6	120.3(5)
C39	C40	P2	123.4(3)	C29	C34	C33	121.0(5)
C39	C40	C35	118.3(4)	C32	C31	C30	121.0(6)
C12	C11	P1	123.9(3)	C37	C38	C39	120.6(5)
C12	C11	C16	118.7(4)	C36	C37	C38	119.7(5)
C16	C11	P1	117.3(3)	C13	C14	C15	120.3(4)
C19	C18	C17	121.3(4)	C31	C32	C33	119.5(5)
C2	C1	Pd1	71.5(2)	C32	C33	C34	120.0(6)
C2	C1	C4	106.6(4)	C43	O5	C42	114.0(11)
C4	C1	Pd1	101.6(3)	O5	C43	C44	104.9(10)
C1	C2	Pd1	69.9(2)	C41	C42	O5	92.7(10)
C1	C2	C3	108.4(4)				

Table S28 Hydrogen Atom Coordinates ($\text{\AA} \times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 3.

Atom	x	y	z	U(eq)
H18	3161.31	-933.12	5062.26	49
H1	-219.76	1826.52	4514.97	48
H2	-444.66	2994.02	5820.68	50
H12	5737.26	1276.83	6614.57	55
H30	3576.53	5681.53	9007.64	69
H10	540.68	-76.33	4393.81	55
H19	2941.25	-2565.75	5598.72	58
H21	2755.01	-845.85	7924.87	60
H24	5244.61	740.93	8446.05	62
H20	2666.77	-2545.4	6995.45	63
H35	815.02	4060.42	7683.74	67
H16	4343.32	3435.24	5322.41	64
H27	5936.94	4668.52	8936.74	58
H6	4129.59	1251.19	4162.31	59
H39	3183.85	2855.88	9399.19	68
H13	7911.9	2518.09	6952.54	78
H9	-367.5	-980.84	2844.92	72
H8	952.33	-759.31	1943.54	82
H26	7665.28	4039.62	9601.6	73
H15	6501.03	4649.07	5667.33	84
H36	-506.02	4000.73	8589.51	82
H25	7323.04	2089.16	9358.85	76
H7	3192.65	359.28	2596.88	79
H34	4545.07	4880.46	6778.24	84
H31	4760.88	7608.92	9234	95
H38	1853.05	2802.84	10297.92	94
H37	-2.67	3352.21	9883.85	86
H14	8276.36	4190.21	6484.4	88
H32	5875.84	8174.1	8270.39	103
H33	5768.33	6809.87	7037.67	110
H43A	188.52	-635.82	9395.76	166
H43B	899.41	-263.91	8695.54	166
H42A	-855.09	-2612.52	8332.89	249
H42B	-101.37	-2106.5	7680.11	249
H44A	3028.38	96.26	9877.7	595
H44B	2263.24	-128.04	10570.01	595
H44C	2305.41	946.35	10161.59	595
H41A	714.95	-3419.69	7676.95	218
H41B	45.92	-3866.72	8369.05	218
H41C	1459.24	-2887.53	8743.92	218

Refinement model description

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

Details:

1. 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

2.a Ternary CH refined with riding coordinates:

C1(H1), C2(H2)

2.b Secondary CH₂ refined with riding coordinates:

C43(H43A,H43B), C42(H42A,H42B)

2.c Aromatic/amide H refined with riding coordinates:

C18(H18), C12(H12), C30(H30), C10(H10), C19(H19), C21(H21), C24(H24),
C20(H20), C35(H35), C16(H16), C27(H27), C6(H6), C39(H39), C13(H13), C9(H9),
C8(H8), C26(H26), C15(H15), C36(H36), C25(H25), C7(H7), C34(H34), C31(H31),
C38(H38), C37(H37), C14(H14), C32(H32), C33(H33)

2.d Idealised Me refined as rotating group:

C44(H44A,H44B,H44C), C41(H41A,H41B,H41C)

XantPhos–Pd–MAH (4)

Single crystals of $C_{43.5}H_{35}ClO_4P_2Pd$ [4•0.5DCM] were selected using a MitEGen loop and paratone oil. A suitable crystal was selected and run on a Bruker APEX-II CCD diffractometer. The crystal was kept at 99.99 K during data collection. Using Olex2,¹² the structure was solved with the olex2.solve¹³ structure solution program using Charge Flipping and refined with the XL¹⁴ refinement package using Least Squares minimization.

Crystal structure determination of [4•0.5DCM]

Crystal Data for $C_{43.5}H_{35}ClO_4P_2Pd$ ($M = 825.50$ g/mol): monoclinic, space group C2/c (no. 15), $a = 24.7326(18)$ Å, $b = 13.2010(8)$ Å, $c = 23.4604(17)$ Å, $\beta = 111.779(2)^\circ$, $V = 7113.0(9)$ Å³, $Z = 8$, $T = 99.99$ K, $\mu(\text{MoK}\alpha) = 0.732$ mm⁻¹, $D_{\text{calc}} = 1.542$ g/cm³, 34983 reflections measured ($3.546^\circ \leq 2\Theta \leq 55.946^\circ$), 8524 unique ($R_{\text{int}} = 0.0645$, $R_{\text{sigma}} = 0.0608$) which were used in all calculations. The final R_1 was 0.0384 ($I > 2\sigma(I)$) and wR_2 was 0.0830 (all data).

Table S29 Crystal data and structure refinement for 4•0.5DCM.

Identification code	4•0.5DCM
Empirical formula	$C_{43.5}H_{35}ClO_4P_2Pd$
Formula weight	825.50
Temperature/K	99.99
Crystal system	monoclinic
Space group	C2/c
$a/\text{\AA}$	24.7326(18)
$b/\text{\AA}$	13.2010(8)
$c/\text{\AA}$	23.4604(17)
$\alpha/^\circ$	90
$\beta/^\circ$	111.779(2)
$\gamma/^\circ$	90
Volume/Å ³	7113.0(9)
Z	8
$\rho_{\text{calc}}/\text{g/cm}^3$	1.542
μ/mm^{-1}	0.732
$F(000)$	3368.0
Crystal size/mm ³	0.15 × 0.05 × 0.05
Radiation	MoKα ($\lambda = 0.71073$)
2θ range for data collection/°	3.546 to 55.946
Index ranges	-32 ≤ h ≤ 32, -17 ≤ k ≤ 8, -30 ≤ l ≤ 30
Reflections collected	34983
Independent reflections	8524 [$R_{\text{int}} = 0.0645$, $R_{\text{sigma}} = 0.0608$]
Data/restraints/parameters	8524/0/467
Goodness-of-fit on F^2	1.019
Final R indexes [$I >= 2\sigma(I)$]	$R_1 = 0.0384$, $wR_2 = 0.0752$
Final R indexes [all data]	$R_1 = 0.0643$, $wR_2 = 0.0830$
Largest diff. peak/hole / e Å ⁻³	0.81/-0.85

Table S30 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 4•0.5DCM. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	$U(\text{eq})$
Pd1	3366.5(2)	3515.7(2)	5120.3(2)	9.69(6)
P1	3468.8(3)	3148.8(5)	4185.6(3)	9.18(15)
P2	2997.3(3)	5167.3(5)	5030.1(3)	9.80(15)
Cl1	5252.3(5)	6999.2(9)	8165.6(5)	53.3(3)
O4	2520.2(8)	4532.6(13)	3752.5(9)	9.9(4)
O2	4485.9(10)	3111.6(16)	6341.6(10)	20.9(5)
O3	4090.6(11)	4306.8(17)	6750.8(10)	27.7(6)
O1	4629.3(10)	1688.7(17)	5894.9(11)	29.0(6)
C5	3887.0(12)	2013(2)	4170.2(13)	11.8(6)
C30	2782.9(12)	2898.1(19)	3547.6(13)	9.2(6)
C36	1510.5(13)	4952(2)	3477.9(13)	11.9(6)
C41	2078.0(12)	4962.2(19)	3902.0(13)	10.1(6)
C33	1683.0(13)	2674(2)	2610.1(13)	13.3(6)
C12	4285.1(13)	4630(2)	4228.7(14)	13.1(6)
C3	4288.2(14)	2258(2)	5966.0(14)	16.0(6)
C16	3606.1(14)	4251(2)	3219.1(14)	17.3(6)
C40	2247.4(12)	5378.6(19)	4486.4(13)	10.4(6)
C11	3802.7(13)	4099(2)	3854.9(13)	11.5(6)
C35	1399.0(13)	4483(2)	2847.7(13)	11.8(6)
C34	1807.4(12)	3574(2)	2949.7(12)	11.2(5)
C17	2950.0(13)	5723(2)	5725.1(13)	12.0(6)
C22	2649.1(14)	5206(2)	6030.2(14)	16.8(6)
C23	3453.6(13)	6068(2)	4827.0(13)	12.0(6)
C6	3822.2(14)	1144(2)	4475.4(14)	18.9(7)
C29	2358.2(12)	3657.2(19)	3403.7(12)	9.7(6)
C37	1088.9(13)	5405(2)	3653.4(14)	14.4(6)
C10	4272.8(13)	1978(2)	3861.3(13)	13.6(6)
C31	2645.4(13)	2028(2)	3189.1(13)	12.8(6)
C39	1812.7(13)	5849(2)	4638.2(14)	13.8(6)
C24	3260.6(13)	6661(2)	4300.9(14)	15.2(6)
C1	3649.2(14)	2258(2)	5736.6(13)	15.4(6)
C19	3095.6(15)	7094(2)	6448.7(15)	21.1(7)
C32	2100.7(13)	1920(2)	2726.9(13)	14.8(6)
C27	4403.2(14)	6835(2)	5115.4(15)	19.0(7)
C8	4518.0(14)	251(2)	4175.1(15)	21.2(7)
C28	4033.1(13)	6158(2)	5231.5(14)	16.3(6)
C9	4589.4(14)	1108(2)	3870.0(14)	19.0(7)
C43	763.8(13)	4199(2)	2513.6(14)	18.1(7)
C4	4008.1(14)	3604(2)	6411.3(13)	17.8(6)
C26	4208.1(15)	7422(2)	4584.3(16)	21.8(7)
C15	3895.8(14)	4912(2)	2972.6(15)	19.8(7)
C42	1576.3(14)	5279(2)	2461.3(14)	17.6(7)
C2	3477.1(14)	3079(2)	6022.2(13)	14.8(6)
C13	4572.8(14)	5293(2)	3975.9(15)	17.8(7)
C38	1241.8(13)	5857(2)	4224.5(14)	15.6(6)
C18	3177.2(14)	6677(2)	5944.8(14)	16.7(6)
C14	4379.7(14)	5431(2)	3348.2(15)	18.3(7)
C25	3640.4(14)	7331(2)	4180.5(15)	19.7(7)
C20	2775.9(14)	6589(2)	6727.5(14)	21.1(7)
C7	4131.2(16)	268(2)	4472.9(15)	24.4(8)
C21	2552.8(15)	5635(2)	6519.3(15)	21.7(7)
C44	5000	6293(4)	7500	49.5(18)

Table S31 Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 4•0.5DCM. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}\mathbf{U}_{11} + 2hka^*\mathbf{b}^*\mathbf{U}_{12} + \dots]$.

Atom	\mathbf{U}_{11}	\mathbf{U}_{22}	\mathbf{U}_{33}	\mathbf{U}_{23}	\mathbf{U}_{13}	\mathbf{U}_{12}
Pd1	11.43(11)	8.67(10)	9.97(10)	0.92(9)	5.12(8)	1.34(9)
P1	10.3(4)	8.7(3)	9.0(4)	0.0(3)	4.1(3)	1.5(3)
P2	10.9(4)	9.2(3)	9.7(4)	-0.1(3)	4.3(3)	0.9(3)
Cl1	45.2(7)	74.4(8)	32.7(6)	-16.0(5)	5.5(5)	2.8(6)
O4	8.0(10)	9.0(9)	12.1(10)	-1.4(8)	3.1(8)	1.1(8)
O2	17.0(12)	22.9(11)	20.8(12)	-3.0(9)	4.6(10)	1.1(10)
O3	31.9(15)	30.3(13)	18.8(12)	-9.3(10)	7.0(11)	1.1(11)
O1	24.3(13)	28.0(13)	33.4(14)	0.6(11)	9.2(12)	12.5(11)
C5	8.4(14)	11.2(13)	12.1(14)	-2.3(11)	-0.6(12)	2.6(11)
C30	10.3(15)	10.0(13)	9.7(14)	1.7(11)	6.5(12)	1.1(11)
C36	13.1(15)	10.0(13)	13.8(15)	2.3(11)	6.2(13)	-1.2(11)
C41	11.6(15)	6.8(12)	13.8(14)	1.7(11)	7.0(12)	1.4(11)
C33	10.9(15)	17.4(14)	10.4(14)	-0.3(12)	2.7(12)	-3.9(12)
C12	15.2(16)	12.5(13)	12.0(14)	0.1(11)	5.4(13)	2.8(12)
C3	20.5(17)	13.9(14)	14.1(15)	2.5(12)	7.2(14)	2.8(13)
C16	12.1(16)	23.7(16)	13.6(15)	3.5(12)	1.9(13)	-2.8(13)
C40	11.0(15)	8.3(13)	11.7(14)	2.7(11)	4.0(12)	1.1(11)
C11	11.6(15)	9.5(13)	13.3(15)	-0.3(11)	4.5(12)	2.2(11)
C35	10.0(14)	13.3(14)	11.7(14)	3.4(11)	3.7(12)	2.0(11)
C34	12.4(14)	13.8(13)	8.5(13)	0.4(11)	5.2(11)	-3.1(12)
C17	12.2(15)	13.2(13)	9.6(14)	0.2(11)	3.0(12)	5.0(11)
C22	21.4(17)	14.0(14)	17.2(16)	2.1(12)	9.7(14)	3.2(13)
C23	11.6(15)	9.4(12)	17.5(15)	-3.3(11)	8.2(13)	-0.7(11)
C6	24.8(18)	15.7(14)	18.9(16)	1.9(12)	11.3(15)	7.5(13)
C29	11.2(14)	9.8(13)	8.7(13)	0.3(10)	4.4(11)	-1.6(11)
C37	10.2(15)	16.0(14)	17.1(16)	3.5(12)	5.3(13)	0.0(12)
C10	10.3(15)	13.1(14)	15.0(15)	-3.3(12)	1.8(13)	0.6(12)
C31	15.2(16)	9.8(13)	15.8(15)	0.6(11)	8.6(13)	0.4(11)
C39	16.3(16)	12.6(14)	14.0(15)	0.4(11)	7.3(13)	2.3(12)
C24	12.1(15)	14.8(15)	17.8(16)	1.8(12)	4.5(13)	1.0(12)
C1	19.7(17)	12.4(14)	15.8(15)	5.0(12)	8.7(14)	0.9(12)
C19	21.8(18)	16.6(15)	22.2(17)	-6.7(13)	5.2(15)	4.8(13)
C32	19.4(17)	12.6(13)	13.8(15)	-3.4(12)	7.9(13)	-4.2(12)
C27	12.3(16)	17.4(14)	27.2(18)	-7.5(13)	7.2(14)	-1.2(13)
C8	19.8(18)	17.5(15)	20.5(17)	-5.4(13)	0.6(14)	8.5(13)
C28	15.3(16)	16.9(14)	16.4(16)	-1.3(12)	5.4(13)	5.5(12)
C9	12.6(16)	23.6(16)	19.6(17)	-10.2(13)	4.5(14)	1.2(13)
C43	12.0(16)	25.0(16)	14.6(16)	-0.9(13)	1.9(13)	-1.2(13)
C4	21.4(17)	22.3(15)	12.0(15)	4.9(13)	8.8(13)	3.9(14)
C26	24.1(19)	12.6(14)	37(2)	-2.9(14)	20.2(17)	-2.0(13)
C15	16.1(17)	26.9(17)	15.9(16)	7.9(13)	5.6(14)	2.0(14)
C42	19.1(17)	20.4(15)	13.7(15)	5.1(12)	6.5(14)	1.0(13)
C2	17.1(16)	17.5(14)	12.5(15)	3.7(12)	8.8(13)	2.1(13)
C13	15.6(17)	15.4(15)	22.0(17)	-3.0(13)	6.6(14)	-3.3(13)
C38	13.9(16)	17.2(15)	19.0(16)	0.7(12)	10.0(14)	4.6(12)
C18	19.1(17)	14.8(15)	16.9(15)	-0.5(12)	7.5(14)	0.9(12)
C14	16.7(17)	14.8(14)	25.4(18)	6.0(13)	10.2(15)	1.2(13)
C25	20.9(18)	17.6(15)	24.3(18)	5.6(13)	12.6(15)	0.5(13)
C20	27.8(18)	23.4(16)	11.6(15)	0.4(13)	7.0(14)	14.1(15)
C7	37(2)	14.1(15)	20.6(17)	2.4(13)	9.5(16)	8.1(14)
C21	27.5(19)	21.7(16)	21.4(18)	7.8(13)	15.3(16)	8.3(14)
C44	97(6)	31(3)	30(3)	0	34(4)	0

Table S32 Bond Lengths for 4•0.5DCM.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pd1	P1	2.3492(7)	C16	C11	1.401(4)
Pd1	P2	2.3427(7)	C16	C15	1.384(4)
Pd1	C1	2.141(3)	C40	C39	1.397(4)
Pd1	C2	2.111(3)	C35	C34	1.529(4)
P1	C5	1.830(3)	C35	C43	1.520(4)
P1	C30	1.829(3)	C35	C42	1.554(4)
P1	C11	1.825(3)	C34	C29	1.388(4)
P2	C40	1.841(3)	C17	C22	1.389(4)
P2	C17	1.831(3)	C17	C18	1.397(4)
P2	C23	1.821(3)	C22	C21	1.377(4)
Cl1	C44	1.724(3)	C23	C24	1.388(4)
O4	C41	1.388(3)	C23	C28	1.400(4)
O4	C29	1.387(3)	C6	C7	1.388(4)
O2	C3	1.402(4)	C37	C38	1.385(4)
O2	C4	1.410(4)	C10	C9	1.385(4)
O3	C4	1.190(4)	C31	C32	1.388(4)
O1	C3	1.187(3)	C39	C38	1.385(4)
C5	C6	1.393(4)	C24	C25	1.393(4)
C5	C10	1.397(4)	C1	C2	1.420(4)
C30	C29	1.399(4)	C19	C18	1.385(4)
C30	C31	1.390(4)	C19	C20	1.372(4)
C36	C41	1.387(4)	C27	C28	1.377(4)
C36	C35	1.531(4)	C27	C26	1.392(4)
C36	C37	1.390(4)	C8	C9	1.385(4)
C41	C40	1.390(4)	C8	C7	1.378(5)
C33	C34	1.399(4)	C4	C2	1.466(4)
C33	C32	1.386(4)	C26	C25	1.377(5)
C12	C11	1.381(4)	C15	C14	1.377(4)
C12	C13	1.392(4)	C13	C14	1.381(4)
C3	C1	1.468(4)	C20	C21	1.389(4)

Table S33 Bond Angles for 4•0.5DCM.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
P2	Pd1	P1	106.32(3)	C43	C35	C34	112.5(2)
C1	Pd1	P1	110.43(8)	C43	C35	C42	109.1(2)
C1	Pd1	P2	143.25(8)	C33	C34	C35	125.7(3)
C2	Pd1	P1	149.39(8)	C29	C34	C33	116.8(3)
C2	Pd1	P2	104.24(8)	C29	C34	C35	117.4(2)
C2	Pd1	C1	39.01(11)	C22	C17	P2	119.0(2)
C5	P1	Pd1	116.42(10)	C22	C17	C18	118.2(3)
C30	P1	Pd1	114.39(9)	C18	C17	P2	122.7(2)
C30	P1	C5	101.25(12)	C21	C22	C17	121.2(3)
C11	P1	Pd1	118.52(9)	C24	C23	P2	124.0(2)
C11	P1	C5	101.92(13)	C24	C23	C28	118.9(3)
C11	P1	C30	101.83(13)	C28	C23	P2	117.1(2)
C40	P2	Pd1	117.54(9)	C7	C6	C5	121.0(3)
C17	P2	Pd1	116.37(9)	O4	C29	C30	115.3(2)
C17	P2	C40	100.11(13)	O4	C29	C34	120.4(2)
C23	P2	Pd1	111.90(9)	C34	C29	C30	124.3(3)
C23	P2	C40	106.41(13)	C38	C37	C36	120.4(3)
C23	P2	C17	102.81(13)	C9	C10	C5	120.7(3)
C29	O4	C41	114.1(2)	C32	C31	C30	120.4(3)
C3	O2	C4	109.4(2)	C38	C39	C40	120.4(3)
C6	C5	P1	119.4(2)	C23	C24	C25	120.2(3)
C6	C5	C10	118.1(3)	C3	C1	Pd1	106.55(19)
C10	C5	P1	122.5(2)	C2	C1	Pd1	69.33(16)
C29	C30	P1	117.0(2)	C2	C1	C3	107.3(3)
C31	C30	P1	126.1(2)	C20	C19	C18	120.4(3)
C31	C30	C29	116.9(3)	C33	C32	C31	121.1(3)
C41	C36	C35	117.9(3)	C28	C27	C26	120.2(3)
C41	C36	C37	117.0(3)	C7	C8	C9	119.6(3)
C37	C36	C35	125.0(3)	C27	C28	C23	120.6(3)
O4	C41	C40	115.7(3)	C8	C9	C10	120.3(3)
C36	C41	O4	119.8(2)	O2	C4	C2	107.8(2)
C36	C41	C40	124.5(3)	O3	C4	O2	119.6(3)
C32	C33	C34	120.4(3)	O3	C4	C2	132.6(3)
C11	C12	C13	120.4(3)	C25	C26	C27	119.6(3)
O2	C3	C1	107.9(2)	C14	C15	C16	120.5(3)
O1	C3	O2	119.8(3)	C1	C2	Pd1	71.66(16)
O1	C3	C1	132.3(3)	C1	C2	C4	107.4(3)
C15	C16	C11	120.4(3)	C4	C2	Pd1	104.36(19)
C41	C40	P2	118.8(2)	C14	C13	C12	120.5(3)
C41	C40	C39	116.6(3)	C37	C38	C39	121.0(3)
C39	C40	P2	124.3(2)	C19	C18	C17	120.5(3)
C12	C11	P1	120.0(2)	C15	C14	C13	119.4(3)
C12	C11	C16	118.7(3)	C26	C25	C24	120.5(3)
C16	C11	P1	121.2(2)	C19	C20	C21	119.8(3)
C36	C35	C42	107.5(2)	C8	C7	C6	120.2(3)
C34	C35	C36	107.1(2)	C22	C21	C20	119.8(3)
C34	C35	C42	108.0(2)	Cl1 ¹	C44	Cl1	114.6(3)
C43	C35	C36	112.3(2)				

¹1-X,+Y,3/2-Z

Table S34 Hydrogen Atom Coordinates ($\text{\AA} \times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 4•0.5DCM.

Atom	x	y	z	U(eq)
H33	1309.93	2578.74	2297.63	16
H12	4421.27	4542.79	4661.19	16
H16	3271.82	3899.45	2955.55	21
H22	2507.01	4543.18	5899.16	20
H6	3562.32	1151.35	4688.81	23
H37	693.53	5404.12	3379.86	17
H10	4318.67	2556.76	3642.9	16
H31	2925.86	1503.29	3260.71	15
H39	1909.24	6164.77	5027.3	17
H24	2868.36	6610.28	4022.15	18
H1	3426.31	1607.37	5650.22	18
H19	3262.13	7733.9	6602.16	25
H32	2012.58	1319.61	2486.56	18
H27	4792.73	6902.86	5398.56	23
H8	4734.48	-345.39	4179.01	25
H28	4172.41	5748.15	5589.48	20
H9	4856.73	1100.25	3665.64	23
H43A	649.02	3699.04	2756.47	27
H43B	712.14	3908.79	2112.15	27
H43C	520.68	4804.95	2456.68	27
H26	4465.03	7881.35	4500.92	26
H15	3759.84	5007.13	2540.77	24
H42A	1338.4	5889.83	2415.03	26
H42B	1514.04	4997.24	2055.37	26
H42C	1988.34	5452.86	2669.83	26
H2	3135.3	3016.59	6150.25	18
H13	4904.75	5653.58	4237.2	21
H38	950.4	6177.61	4334.27	19
H18	3389.18	7042.29	5747.12	20
H14	4578.89	5880.89	3177.14	22
H25	3506.65	7728.7	3817.04	24
H20	2707.15	6890.92	7062.04	25
H7	4075.92	-322.36	4676.83	29
H21	2334.53	5279.57	6713.72	26
H44A	5318.84	5850.41	7488.73	59
H44B	4681.16	5850.4	7511.26	59

Table S35 Atomic Occupancy for 4•0.5DCM.

Atom	<i>Occupancy</i>	Atom	<i>Occupancy</i>	Atom	<i>Occupancy</i>
H44A	0.5	H44B			0.5

Refinement model description

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

Details:

1. 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

2. Others

Fixed Sof: H44A(0.5) H44B(0.5)

3.a Ternary CH refined with riding coordinates:

C1(H1), C2(H2)

3.b Secondary CH2 refined with riding coordinates:

C44(H44A,H44B)

3.c Aromatic/amide H refined with riding coordinates:

C33(H33), C12(H12), C16(H16), C22(H22), C6(H6), C37(H37), C10(H10), C31(H31),
C39(H39), C24(H24), C19(H19), C32(H32), C27(H27), C8(H8), C28(H28), C9(H9),
C26(H26), C15(H15), C13(H13), C38(H38), C18(H18), C14(H14), C25(H25), C20(H20),
C7(H7), C21(H21)

3.d Idealised Me refined as rotating group:

C43(H43A,H43B,H43C), C42(H42A,H42B,H42C)

dppf-Pd-MAH (5)

Single crystals of $C_{38}H_{30}FeO_3P_2Pd$ [5] were selected using a MiteEGen loop using paratone oil. A suitable crystal was selected and run on Bruker APEX-II CCD diffractometer. The crystal was kept at 273.15 K during data collection. Using Olex2,¹² the structure was solved with the olex2.solve¹³ structure solution program using Charge Flipping and refined with the XL¹⁴ refinement package using Least Squares minimization.

Crystal structure determination of [5]

Crystal Data for $C_{38}H_{30}FeO_3P_2Pd$ ($M = 758.81$ g/mol): monoclinic, space group Cc (no. 9), $a = 26.339(12)$ Å, $b = 8.380(4)$ Å, $c = 17.649(9)$ Å, $\beta = 124.36(2)^\circ$, $V = 3216(3)$ Å³, $Z = 4$, $T = 273.15$ K, $\mu(\text{MoK}\alpha) = 1.147$ mm⁻¹, $D_{\text{calc}} = 1.567$ g/cm³, 52738 reflections measured ($5.21^\circ \leq 2\Theta \leq 56.218^\circ$), 7730 unique ($R_{\text{int}} = 0.1286$, $R_{\text{sigma}} = 0.1243$) which were used in all calculations. The final R_1 was 0.1147 ($I > 2\sigma(I)$) and wR_2 was 0.1548 (all data).

Table S36 Crystal data and structure refinement for 5.

Identification code	5
Empirical formula	$C_{38}H_{30}FeO_3P_2Pd$
Formula weight	758.81
Temperature/K	273.15
Crystal system	monoclinic
Space group	Cc
$a/\text{\AA}$	26.339(12)
$b/\text{\AA}$	8.380(4)
$c/\text{\AA}$	17.649(9)
$\alpha/^\circ$	90
$\beta/^\circ$	124.36(2)
$\gamma/^\circ$	90
Volume/Å ³	3216(3)
Z	4
$\rho_{\text{calc}}/\text{g/cm}^3$	1.567
μ/mm^{-1}	1.147
F(000)	1536.0
Crystal size/mm ³	0.075 × 0.05 × 0.05
Radiation	MoKα ($\lambda = 0.71073$)
2θ range for data collection/°	5.21 to 56.218
Index ranges	-34 ≤ h ≤ 34, -11 ≤ k ≤ 11, -23 ≤ l ≤ 23
Reflections collected	52738
Independent reflections	7730 [$R_{\text{int}} = 0.1286$, $R_{\text{sigma}} = 0.1243$]
Data/restraints/parameters	7730/2/407
Goodness-of-fit on F^2	1.271
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.1147$, $wR_2 = 0.1435$
Final R indexes [all data]	$R_1 = 0.1594$, $wR_2 = 0.1548$
Largest diff. peak/hole / e Å ⁻³	2.56/-1.19
Flack parameter	0.06(6)

**Table S37 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$)
for 5. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.**

Atom	x	y	z	$U(\text{eq})$
Pd1	5058.1(4)	8481.8(11)	5028.7(5)	28.4(3)
Fe1	5060.9(9)	4843(2)	6678.4(13)	32.0(5)
P1	4256.5(16)	6750(5)	4639(2)	30.6(9)
P2	5876.0(16)	7608(4)	6434(2)	27.5(8)
O2	5311(7)	9438(16)	3513(9)	73(4)
O1	4289(8)	9721(18)	2511(10)	92(5)
C10	3766(8)	9190(20)	5093(12)	46(4)
C28	6964(7)	5861(18)	7090(11)	41(4)
C23	5205(7)	7050(17)	7225(10)	34(3)
C27	6384(7)	6241(16)	6338(10)	32(4)
C5	3659(6)	7701(16)	4701(8)	27(3)
C25	5638(8)	4760(20)	8071(9)	50(5)
C17	4435(6)	4945(17)	5308(9)	34(3)
C33	6394(6)	9214(17)	7177(10)	33(3)
C11	3827(6)	5970(19)	3458(9)	31(3)
C34	6350(7)	9846(17)	7857(10)	38(4)
C3	4713(11)	9868(19)	3272(13)	60(5)
C32	6178(8)	5570(19)	5503(10)	47(4)
C1	4787(8)	10441(19)	4098(11)	48(4)
C2	5413(8)	10527(19)	4791(11)	48(4)
C38	6821(7)	9832(18)	7033(12)	45(4)
C26	5964(7)	5154(18)	7680(10)	42(4)
C12	3847(7)	4440(20)	3241(11)	52(5)
C22	5701(6)	6596(18)	7160(9)	35(3)
C37	7192(8)	11047(19)	7572(13)	54(5)
C8	2782(8)	9230(20)	4840(11)	53(5)
C7	2670(7)	7770(20)	4474(10)	48(4)
C21	4151(7)	4340(20)	5739(11)	50(4)
C24	5186(7)	5930(20)	7809(11)	49(4)
C29	7327(8)	4820(20)	7002(14)	56(5)
C31	6552(10)	4500(30)	5430(13)	74(6)
C6	3098(7)	6982(19)	4408(10)	44(4)
C4	5737(11)	9940(20)	4398(14)	64(5)
C9	3331(8)	10000(20)	5147(12)	59(5)
C18	4926(6)	3889(16)	5528(9)	33(3)
C15	3157(9)	6510(30)	1850(12)	74(6)
C19	4936(8)	2664(18)	6092(11)	48(4)
C14	3180(9)	5000(30)	1652(13)	73(7)
C35	6734(8)	11085(18)	8385(12)	53(4)
C30	7129(10)	4140(20)	6190(15)	71(6)
O3	6282(8)	9820(20)	4738(12)	104(6)
C36	7152(7)	11690(20)	8237(13)	56(5)
C20	4475(8)	2945(19)	6226(11)	55(5)
C16	3484(8)	7060(20)	2756(12)	65(5)
C13	3536(9)	3940(30)	2352(14)	69(6)

Table S38 Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 5. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^2U_{11} + 2hka^*b^*U_{12} + \dots]$.

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Pd1	29.3(5)	31.0(5)	28.4(5)	7.2(6)	18.4(4)	6.8(6)
Fe1	35.3(11)	32.6(12)	27.1(11)	-0.3(9)	16.9(9)	-5.5(9)
P1	31(2)	30(2)	29(2)	-2.9(17)	15.3(17)	2.6(17)
P2	25.7(18)	30(2)	28.6(19)	2.4(16)	16.6(16)	1.7(16)
O2	101(11)	81(10)	65(9)	-2(8)	65(9)	3(9)
O1	129(13)	91(11)	42(8)	4(8)	40(9)	-3(10)
C10	37(9)	52(10)	52(11)	-12(9)	27(9)	2(8)
C28	36(9)	42(9)	44(10)	6(8)	21(8)	3(7)
C23	38(8)	35(8)	39(9)	-11(7)	27(7)	-6(7)
C27	35(8)	30(8)	40(9)	6(7)	27(8)	-2(7)
C5	29(8)	31(8)	10(6)	-10(6)	3(6)	-1(6)
C25	61(11)	67(12)	16(8)	1(8)	17(8)	-21(10)
C17	37(9)	31(8)	26(8)	-3(6)	13(7)	-5(7)
C33	34(8)	32(8)	34(8)	8(7)	19(7)	10(7)
C11	25(8)	52(10)	12(7)	-10(7)	9(6)	-6(7)
C34	39(9)	29(8)	50(10)	-3(7)	27(8)	-4(7)
C3	105(16)	32(9)	41(11)	4(9)	39(12)	-9(11)
C32	67(11)	51(10)	30(9)	11(8)	31(8)	18(9)
C1	68(13)	33(9)	50(11)	6(8)	38(10)	12(8)
C2	68(12)	32(9)	53(11)	9(8)	40(10)	7(8)
C38	49(10)	35(9)	65(11)	8(8)	41(9)	-4(8)
C26	50(10)	43(9)	32(8)	11(7)	23(8)	4(8)
C12	39(9)	64(12)	41(10)	-22(9)	15(8)	5(8)
C22	34(8)	35(8)	32(8)	-4(7)	17(7)	-7(7)
C37	52(10)	35(9)	82(14)	2(9)	42(11)	-8(8)
C8	44(10)	78(13)	42(10)	-15(10)	27(8)	0(10)
C7	26(8)	79(13)	38(10)	0(9)	18(8)	-4(8)
C21	34(9)	52(11)	51(10)	3(9)	15(8)	-21(8)
C24	45(10)	67(12)	49(10)	-25(9)	35(9)	-21(9)
C29	39(10)	57(12)	67(13)	16(10)	28(10)	11(8)
C31	111(17)	89(15)	50(11)	3(11)	63(13)	34(13)
C6	44(10)	42(10)	33(9)	-11(7)	14(8)	-8(8)
C4	92(16)	63(12)	60(13)	6(10)	57(13)	10(12)
C9	55(12)	57(12)	65(12)	-21(9)	34(10)	0(10)
C18	36(8)	31(8)	27(7)	-11(6)	14(7)	-2(6)
C15	78(14)	100(18)	35(10)	13(12)	26(10)	4(14)
C19	59(11)	26(9)	40(9)	3(7)	17(9)	7(8)
C14	51(12)	140(20)	36(11)	-31(13)	28(10)	-21(13)
C35	60(11)	36(10)	60(11)	-8(8)	32(9)	-3(8)
C30	84(15)	80(14)	76(14)	32(12)	61(13)	52(12)
O3	89(12)	150(17)	109(13)	10(12)	77(11)	16(12)
C36	49(10)	25(9)	85(13)	-8(9)	33(10)	-16(8)
C20	74(13)	40(10)	41(10)	-3(8)	27(9)	-33(9)
C16	78(13)	70(13)	44(11)	2(10)	33(10)	6(11)
C13	60(12)	77(14)	73(14)	-36(12)	40(12)	-7(11)

Table S39 Bond Lengths for 5.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pd1	P1	2.324(4)	C25	C26	1.41(2)
Pd1	P2	2.302(4)	C25	C24	1.41(2)
Pd1	C1	2.140(16)	C17	C21	1.43(2)
Pd1	C2	2.105(16)	C17	C18	1.429(19)
Fe1	C23	2.020(14)	C33	C34	1.38(2)
Fe1	C25	2.034(14)	C33	C38	1.39(2)
Fe1	C17	2.019(13)	C11	C12	1.34(2)
Fe1	C26	2.025(15)	C11	C16	1.39(2)
Fe1	C22	2.026(14)	C34	C35	1.38(2)
Fe1	C21	2.047(15)	C3	C1	1.44(2)
Fe1	C24	2.045(15)	C32	C31	1.39(2)
Fe1	C18	2.019(13)	C1	C2	1.39(2)
Fe1	C19	2.032(16)	C2	C4	1.46(2)
Fe1	C20	2.038(15)	C38	C37	1.36(2)
P1	C5	1.822(14)	C26	C22	1.44(2)
P1	C17	1.809(14)	C12	C13	1.36(2)
P1	C11	1.842(14)	C37	C36	1.35(2)
P2	C27	1.840(15)	C8	C7	1.33(2)
P2	C33	1.836(15)	C8	C9	1.38(2)
P2	C22	1.800(14)	C7	C6	1.37(2)
O2	C3	1.43(2)	C21	C20	1.41(2)
O2	C4	1.38(2)	C29	C30	1.34(3)
O1	C3	1.17(2)	C31	C30	1.38(3)
C10	C5	1.37(2)	C4	O3	1.21(2)
C10	C9	1.38(2)	C18	C19	1.42(2)
C28	C27	1.38(2)	C15	C14	1.32(3)
C28	C29	1.37(2)	C15	C16	1.40(3)
C23	C22	1.426(19)	C19	C20	1.38(2)
C23	C24	1.42(2)	C14	C13	1.38(3)
C27	C32	1.37(2)	C35	C36	1.37(2)
C5	C6	1.40(2)			

Table S40 Bond Angles for 5.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
P2	Pd1	P1	105.16(13)	C10	C5	P1	119.2(11)
C1	Pd1	P1	113.5(5)	C10	C5	C6	116.8(14)
C1	Pd1	P2	140.8(5)	C6	C5	P1	123.9(11)
C2	Pd1	P1	151.8(5)	C26	C25	Fe1	69.3(8)
C2	Pd1	P2	102.9(5)	C24	C25	Fe1	70.2(9)
C2	Pd1	C1	38.3(6)	C24	C25	C26	108.0(14)
C23	Fe1	C25	69.2(7)	P1	C17	Fe1	123.5(7)
C23	Fe1	C26	69.7(6)	C21	C17	Fe1	70.5(8)
C23	Fe1	C22	41.3(6)	C21	C17	P1	128.6(12)
C23	Fe1	C21	113.3(7)	C18	C17	Fe1	69.3(8)
C23	Fe1	C24	40.8(6)	C18	C17	P1	123.9(11)
C23	Fe1	C19	176.9(7)	C18	C17	C21	107.5(13)
C23	Fe1	C20	143.0(7)	C34	C33	P2	120.8(11)
C25	Fe1	C21	134.9(6)	C34	C33	C38	119.5(14)
C25	Fe1	C24	40.4(7)	C38	C33	P2	119.7(12)
C25	Fe1	C20	109.2(7)	C12	C11	P1	124.2(12)

C17	Fe1	C23	109.9(6)	C12	C11	C16	118.9(14)
C17	Fe1	C25	175.7(7)	C16	C11	P1	116.8(13)
C17	Fe1	C26	143.4(6)	C33	C34	C35	119.3(15)
C17	Fe1	C22	113.3(6)	O2	C3	C1	106.6(16)
C17	Fe1	C21	41.2(6)	O1	C3	O2	119.5(18)
C17	Fe1	C24	136.3(7)	O1	C3	C1	134(2)
C17	Fe1	C18	41.4(6)	C27	C32	C31	119.5(15)
C17	Fe1	C19	68.9(6)	C3	C1	Pd1	108.5(11)
C17	Fe1	C20	68.8(6)	C2	C1	Pd1	69.5(9)
C26	Fe1	C25	40.7(6)	C2	C1	C3	108.9(17)
C26	Fe1	C22	41.5(6)	C1	C2	Pd1	72.2(10)
C26	Fe1	C21	174.3(6)	C1	C2	C4	106.6(16)
C26	Fe1	C24	68.2(6)	C4	C2	Pd1	105.2(11)
C26	Fe1	C19	109.4(7)	C37	C38	C33	119.3(16)
C26	Fe1	C20	134.3(7)	C25	C26	Fe1	70.0(9)
C22	Fe1	C25	69.0(6)	C25	C26	C22	107.8(14)
C22	Fe1	C21	143.8(6)	C22	C26	Fe1	69.3(8)
C22	Fe1	C24	68.3(6)	C11	C12	C13	121.9(18)
C22	Fe1	C19	136.2(7)	P2	C22	Fe1	122.0(7)
C22	Fe1	C20	175.1(7)	C23	C22	Fe1	69.1(8)
C24	Fe1	C21	110.6(7)	C23	C22	P2	123.1(11)
C18	Fe1	C23	136.2(6)	C23	C22	C26	107.8(13)
C18	Fe1	C25	142.0(7)	C26	C22	Fe1	69.2(9)
C18	Fe1	C26	112.4(6)	C26	C22	P2	128.8(11)
C18	Fe1	C22	109.9(6)	C36	C37	C38	121.9(16)
C18	Fe1	C21	69.1(7)	C7	C8	C9	120.9(16)
C18	Fe1	C24	176.8(7)	C8	C7	C6	120.9(16)
C18	Fe1	C19	41.0(6)	C17	C21	Fe1	68.4(8)
C18	Fe1	C20	68.4(7)	C20	C21	Fe1	69.4(9)
C19	Fe1	C25	112.3(7)	C20	C21	C17	107.4(15)
C19	Fe1	C21	67.8(7)	C23	C24	Fe1	68.7(8)
C19	Fe1	C24	142.0(7)	C25	C24	Fe1	69.4(9)
C19	Fe1	C20	39.7(7)	C25	C24	C23	109.2(13)
C20	Fe1	C21	40.5(7)	C30	C29	C28	121.1(17)
C20	Fe1	C24	113.5(7)	C30	C31	C32	120.1(16)
C5	P1	Pd1	112.3(5)	C7	C6	C5	120.8(15)
C5	P1	C11	103.0(6)	O2	C4	C2	108.8(18)
C17	P1	Pd1	118.1(5)	O3	C4	O2	121.2(18)
C17	P1	C5	104.0(7)	O3	C4	C2	130(2)
C17	P1	C11	102.1(7)	C10	C9	C8	117.8(17)
C11	P1	Pd1	115.5(5)	C17	C18	Fe1	69.3(8)
C27	P2	Pd1	112.7(5)	C19	C18	Fe1	70.0(8)
C33	P2	Pd1	113.7(5)	C19	C18	C17	107.1(13)
C33	P2	C27	103.7(6)	C14	C15	C16	122(2)
C22	P2	Pd1	117.2(5)	C18	C19	Fe1	69.0(8)
C22	P2	C27	105.3(7)	C20	C19	Fe1	70.4(9)
C22	P2	C33	102.9(7)	C20	C19	C18	109.1(14)
C4	O2	C3	108.5(14)	C15	C14	C13	119.5(17)
C5	C10	C9	122.6(16)	C36	C35	C34	120.7(17)
C29	C28	C27	120.2(16)	C29	C30	C31	119.8(16)
C22	C23	Fe1	69.6(8)	C37	C36	C35	119.2(16)
C24	C23	Fe1	70.6(9)	C21	C20	Fe1	70.1(8)
C24	C23	C22	107.1(14)	C19	C20	Fe1	69.9(9)
C28	C27	P2	121.5(12)	C19	C20	C21	109.0(14)
C32	C27	P2	119.1(11)	C11	C16	C15	118.3(19)
C32	C27	C28	119.4(14)	C12	C13	C14	119.6(19)

Table S41 Hydrogen Atom Coordinates ($\text{\AA} \times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 5.

Atom	x	y	z	U(eq)
H10	4146.01	9663.36	5331.57	55
H28	7107.54	6314.58	7658.6	50
H23	4943.88	7917.24	6937.47	41
H25	5710.21	3872.05	8437.55	61
H34	6065.74	9442.75	7960.86	46
H32	5790.29	5826.57	4989.32	56
H1	4506.03	11253.68	4060.19	57
H2	5579.14	11414.74	5228.57	57
H38	6853.42	9420.47	6572.07	54
H26	6289.82	4585.43	7746.22	50
H12	4080.03	3711.66	3709.76	62
H37	7482.69	11447.22	7479.32	65
H8	2487.8	9731.14	4889.92	64
H7	2294.39	7281.19	4260.35	58
H21	3814.28	4774.38	5705.73	60
H24	4916.28	5967.07	7991.47	59
H29	7718.12	4577.43	7511.7	67
H31	6412.3	4031.88	4867.38	89
H6	3014.67	5955.63	4165.72	53
H9	3404.72	11028.52	5381.81	71
H18	5190.2	3985.33	5337.71	40
H15	2917.6	7229.83	1373.61	89
H19	5208.9	1809.28	6332.25	58
H14	2957.63	4662.53	1044.47	87
H35	6706.74	11515.12	8846.88	64
H30	7380.05	3430.99	6140.27	86
H36	7406.41	12530.66	8590.04	67
H20	4392.41	2320.36	6579.33	66
H16	3472.62	8133.17	2884.77	77
H13	3564.26	2881.34	2219.64	83

Refinement model description

Number of restraints - 2, number of constraints - unknown.

Details:

1. Twinned data refinement

Scales: 0.94(6)

0.06(6)

2. Fixed Uiso

At 1.2 times of:

All C(H) groups

3.a Ternary CH refined with riding coordinates:

C1(H1), C2(H2)

3.b Aromatic/amide H refined with riding coordinates:

C10(H10), C28(H28), C23(H23), C25(H25), C34(H34), C32(H32), C38(H38),
C26(H26), C12(H12), C37(H37), C8(H8), C7(H7), C21(H21), C24(H24), C29(H29),
C31(H31), C6(H6), C9(H9), C18(H18), C15(H15), C19(H19), C14(H14), C35(H35),
C30(H30), C36(H36), C20(H20), C16(H16), C13(H13)

XPhos-Pd-MAH (8)

Single crystals of $C_{37}H_{51}O_3PPd$ [8] were selected using a MiteEgen loop on a Bruker APEX-II CCD diffractometer. The crystal was kept at 273.15 K during data collection. Using Olex2,¹² the structure was solved with the olex2.solve¹³ structure solution program using Charge Flipping and refined with the XL¹⁴ refinement package using Least Squares minimization.

Crystal structure determination of [8]

Crystal Data for $C_{37}H_{51}O_3PPd$ ($M = 680.14$ g/mol): orthorhombic, space group Pbca (no. 61), $a = 18.282(4)$ Å, $b = 18.506(4)$ Å, $c = 20.018(4)$ Å, $V = 6773(2)$ Å³, $Z = 8$, $T = 273.15$ K, $\mu(\text{MoK}\alpha) = 0.629$ mm⁻¹, $D_{\text{calc}} = 1.334$ g/cm³, 193553 reflections measured ($5.136^\circ \leq 2\theta \leq 52.968^\circ$), 6977 unique ($R_{\text{int}} = 0.0435$, $R_{\text{sigma}} = 0.0163$) which were used in all calculations. The final R_1 was 0.0415 ($I > 2\sigma(I)$) and wR_2 was 0.1104 (all data).

Table S42 Crystal data and structure refinement for 8.

Identification code	8
Empirical formula	$C_{37}H_{51}O_3PPd$
Formula weight	680.14
Temperature/K	273.15
Crystal system	orthorhombic
Space group	Pbca
$a/\text{\AA}$	18.282(4)
$b/\text{\AA}$	18.506(4)
$c/\text{\AA}$	20.018(4)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
Volume/Å ³	6773(2)
Z	8
$\rho_{\text{calc}}\text{g}/\text{cm}^3$	1.334
μ/mm^{-1}	0.629
F(000)	2856.0
Crystal size/mm ³	0.175 × 0.15 × 0.15
Radiation	MoKα ($\lambda = 0.71073$)
2θ range for data collection/°	5.136 to 52.968
Index ranges	-22 ≤ h ≤ 22, -23 ≤ k ≤ 23, -25 ≤ l ≤ 24
Reflections collected	193553
Independent reflections	6977 [$R_{\text{int}} = 0.0435$, $R_{\text{sigma}} = 0.0163$]
Data/restraints/parameters	6977/105/440
Goodness-of-fit on F^2	1.118
Final R indexes [$I >= 2\sigma(I)$]	$R_1 = 0.0415$, $wR_2 = 0.0946$
Final R indexes [all data]	$R_1 = 0.0624$, $wR_2 = 0.1104$
Largest diff. peak/hole / e Å ⁻³	0.54/-0.93

Table S43 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 8. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	$U(\text{eq})$
Pd1	4763.2(2)	6520.8(2)	5850.6(2)	43.50(10)
P1	3706.0(4)	7089.5(4)	5517.6(4)	36.53(18)
C23	4238.0(16)	6607.3(16)	6929.6(14)	35.0(6)
C24	4894.9(17)	6977.2(18)	7098.8(16)	39.9(7)
C22	3533.6(16)	7026.3(16)	6883.6(14)	35.1(6)
O2	6398.5(16)	6896(2)	5315.1(17)	89.9(10)
C17	3234.7(15)	7306.0(16)	6296.3(14)	34.4(6)
C28	4230.5(17)	5844.9(17)	6985.4(16)	41.2(7)
C25	5492.4(19)	6584.4(19)	7335.5(18)	48.1(8)
C29	4934.9(18)	7797.8(18)	7112.0(17)	44.4(8)
O1	6814.2(18)	6378(2)	6248.4(19)	99.7(12)
C19	2266.5(19)	7857(2)	6928.7(19)	54.0(9)
C18	2601.2(17)	7723.5(18)	6327.3(17)	46.0(8)
C32	3546.9(18)	5412.0(19)	6839.6(18)	48.7(8)
C21	3167.6(19)	7154(2)	7482.6(17)	51.2(8)
C26	5473.4(19)	5848(2)	7425.1(19)	52.3(9)
C20	2541(2)	7565(2)	7507.1(18)	58.1(9)
C5	3731(2)	7962.6(18)	5075.4(15)	46.0(8)
C27	4848.0(19)	5490.8(19)	7234.5(19)	51.5(8)
O3	5839(2)	7085(3)	4340(2)	138(2)
C35	6150(2)	5468(2)	7702(2)	69.8(12)
C30	5594(2)	8089(2)	6733(2)	61.8(10)
C12	3390(7)	6148(9)	4456(8)	63(3)
C1	5423(2)	6139(3)	5084(2)	72.2(13)
C31	4936(3)	8062(2)	7834(2)	70.2(12)
C2	5740(2)	5914(2)	5689(2)	65.8(11)
C33	3673(2)	4839(2)	6306(2)	66.8(11)
C34	3243(2)	5078(3)	7475(2)	75.5(12)
C11	3025(5)	6660(6)	4936(5)	54(2)
C6	4047(3)	7896(2)	4374.6(18)	64.4(11)
C3	6361(2)	6379(3)	5823(2)	72.3(13)
C36	6385(3)	5779(3)	8357(3)	97.1(17)
C15	1811(7)	6209(6)	4643(6)	61(3)
C7	4079(3)	8627(3)	4029(2)	77.1(13)
C8	4486(3)	9178(3)	4435(2)	88.6(16)
C10	4149(3)	8516(2)	5477.4(19)	66.3(11)
C4	5860(2)	6742(4)	4841(2)	89.8(17)
C9	4156(3)	9246(2)	5122(2)	87.7(15)
C37	6108(3)	4677(3)	7705(4)	133(3)
C16	2337(4)	6785(4)	4911(4)	45.7(19)
C14	2146(5)	5788(6)	4099(5)	65(2)
C13	2841(6)	5820(7)	3959(5)	79(3)
C11A	3052(4)	6436(4)	5139(4)	46(2)
C16A	2420(4)	6270(5)	5279(4)	70(3)
C15A	1851(6)	5972(6)	4788(5)	71(4)
C14A	2216(6)	5480(7)	4301(6)	91(4)
C13A	2832(5)	5405(4)	4348(4)	68(3)
C12A	3398(6)	5987(6)	4580(6)	61(4)

Table S44 Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 8. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^*^2U_{11} + 2hka^*b^*U_{12} + \dots]$.

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Pd1	35.87(14)	55.50(17)	39.11(15)	-7.68(11)	2.99(10)	11.26(11)
P1	35.4(4)	42.1(4)	32.1(4)	-6.7(3)	-0.3(3)	3.9(3)
C23	32.6(15)	43.3(17)	28.9(14)	-1.3(12)	-1.2(12)	5.7(13)
C24	37.0(16)	43.7(18)	39.1(16)	0.6(14)	-4.3(13)	5.2(13)
C22	31.6(14)	37.6(16)	36.1(15)	-6.0(12)	-0.9(12)	2.4(12)
O2	51.1(17)	142(3)	77(2)	-6(2)	3.9(16)	-10.1(19)
C17	29.9(14)	37.4(16)	35.8(15)	-4.6(13)	3.6(12)	2.6(12)
C28	38.1(16)	42.4(17)	43.2(17)	-5.2(14)	-2.0(14)	4.7(14)
C25	37.4(16)	53(2)	54(2)	-0.2(16)	-13.1(15)	2.3(15)
C29	43.2(17)	44.7(18)	45.2(18)	-0.8(15)	-10.1(14)	2.2(14)
O1	57.9(19)	152(4)	89(2)	-26(2)	-23.4(18)	18(2)
C19	40.5(18)	54(2)	67(2)	-4.4(18)	13.0(17)	15.3(16)
C18	38.9(17)	48.4(19)	50.6(19)	2.2(16)	0.7(15)	10.3(14)
C32	43.6(18)	44.8(19)	58(2)	1.7(16)	-7.9(16)	1.3(15)
C21	46.8(19)	70(2)	37.1(16)	-1.1(17)	5.3(15)	11.5(17)
C26	45.3(18)	51(2)	61(2)	0.1(17)	-12.6(17)	10.2(16)
C20	50.9(19)	74(3)	49.6(19)	-6.6(19)	18.0(17)	12.4(19)
C5	55(2)	48.7(19)	33.7(16)	-0.5(14)	-2.6(14)	4.5(16)
C27	51(2)	41.8(18)	62(2)	3.1(16)	-8.5(17)	10.6(16)
O3	76(2)	266(6)	73(2)	46(3)	17(2)	-8(3)
C35	52(2)	65(3)	92(3)	13(2)	-19(2)	15(2)
C30	51(2)	63(2)	72(3)	10(2)	-10.8(19)	-9.4(19)
C12	65(5)	66(6)	59(5)	-20(5)	1(4)	-4(4)
C1	39.1(19)	117(4)	60(2)	-43(3)	10.0(18)	13(2)
C31	95(3)	54(2)	62(2)	-10(2)	-14(2)	2(2)
C2	43(2)	74(3)	81(3)	-25(2)	3.0(19)	22.4(19)
C33	72(3)	52(2)	77(3)	-10(2)	-9(2)	-5(2)
C34	64(3)	87(3)	75(3)	13(3)	4(2)	-10(2)
C11	54(4)	52(5)	54(5)	-9(4)	-6(4)	0(4)
C6	85(3)	70(3)	38.0(18)	-2.4(18)	6.5(19)	-5(2)
C3	44(2)	109(4)	64(3)	-27(3)	2(2)	20(2)
C36	84(3)	124(4)	83(3)	11(3)	-35(3)	28(3)
C15	60(4)	62(5)	60(5)	0(4)	-20(4)	-4(4)
C7	98(4)	91(3)	43(2)	15(2)	0(2)	-15(3)
C8	116(4)	84(3)	66(3)	21(3)	-4(3)	-40(3)
C10	94(3)	62(2)	42(2)	1.1(18)	-6(2)	-16(2)
C4	48(2)	171(6)	50(2)	-9(3)	12(2)	10(3)
C9	135(5)	63(3)	65(3)	0(2)	-5(3)	-27(3)
C37	82(4)	72(3)	244(9)	23(4)	-66(5)	23(3)
C16	47(3)	41(3)	49(4)	1(3)	-16(3)	10(3)
C14	73(4)	65(4)	56(4)	-10(4)	-29(3)	-3(4)
C13	91(4)	82(5)	65(4)	-26(4)	-7(4)	-12(4)
C11A	42(4)	41(4)	54(5)	-11(4)	-16(4)	8(3)
C16A	71(6)	78(6)	62(5)	-25(5)	11(4)	-24(5)
C15A	63(6)	87(8)	64(6)	-7(6)	-4(5)	-33(6)
C14A	91(4)	90(4)	90(4)	-0.9(10)	0.2(10)	-1.8(10)
C13A	96(7)	46(4)	60(5)	-25(4)	-15(5)	25(4)
C12A	69(6)	55(6)	60(7)	-26(5)	-22(5)	18(5)

Table S45 Bond Lengths for 8.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pd1	P1	2.2995(9)	C32	C34	1.520(5)
Pd1	C23	2.369(3)	C21	C20	1.376(5)
Pd1	C24	2.648(3)	C26	C27	1.375(5)
Pd1	C1	2.077(3)	C26	C35	1.528(5)
Pd1	C2	2.135(3)	C5	C6	1.522(5)
P1	C17	1.826(3)	C5	C10	1.510(5)
P1	C5	1.843(3)	O3	C4	1.188(6)
P1	C11	1.881(9)	C35	C36	1.495(7)
P1	C11A	1.862(7)	C35	C37	1.465(7)
C23	C24	1.423(4)	C12	C11	1.505(11)
C23	C22	1.506(4)	C12	C13	1.538(12)
C23	C28	1.415(4)	C1	C2	1.406(6)
C24	C25	1.395(4)	C1	C4	1.454(8)
C24	C29	1.521(5)	C2	C3	1.449(6)
C22	C17	1.396(4)	C11	C16	1.281(10)
C22	C21	1.393(4)	C6	C7	1.521(6)
O2	C3	1.398(6)	C15	C16	1.532(11)
O2	C4	1.397(6)	C15	C14	1.473(12)
C17	C18	1.394(4)	C7	C8	1.501(6)
C28	C32	1.513(5)	C8	C9	1.508(7)
C28	C27	1.397(4)	C10	C9	1.527(6)
C25	C26	1.375(5)	C14	C13	1.303(11)
C29	C30	1.523(5)	C11A	C16A	1.229(9)
C29	C31	1.526(5)	C11A	C12A	1.530(10)
O1	C3	1.188(5)	C16A	C15A	1.535(10)
C19	C18	1.373(5)	C15A	C14A	1.491(11)
C19	C20	1.373(5)	C14A	C13A	1.140(11)
C32	C33	1.523(5)	C13A	C12A	1.563(11)

Table S46 Bond Angles for 8.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
P1	Pd1	C23	83.84(7)	C28	C32	C34	110.9(3)
P1	Pd1	C24	101.77(7)	C34	C32	C33	111.1(3)
C23	Pd1	C24	32.35(10)	C20	C21	C22	121.6(3)
C1	Pd1	P1	115.45(13)	C25	C26	C35	118.9(3)
C1	Pd1	C23	158.84(16)	C27	C26	C25	117.5(3)
C1	Pd1	C24	138.86(13)	C27	C26	C35	123.6(3)
C1	Pd1	C2	38.98(17)	C19	C20	C21	119.5(3)
C2	Pd1	P1	154.17(12)	C6	C5	P1	112.4(3)
C2	Pd1	C23	120.86(14)	C10	C5	P1	110.5(2)
C2	Pd1	C24	103.58(13)	C10	C5	C6	110.7(3)
C17	P1	Pd1	104.45(10)	C26	C27	C28	123.1(3)
C17	P1	C5	103.26(14)	C36	C35	C26	111.9(4)
C17	P1	C11	108.0(3)	C37	C35	C26	114.7(4)
C17	P1	C11A	100.8(3)	C37	C35	C36	113.4(5)
C5	P1	Pd1	121.33(12)	C11	C12	C13	111.8(9)
C5	P1	C11	95.2(4)	C2	C1	Pd1	72.7(2)
C5	P1	C11A	112.9(3)	C2	C1	C4	106.8(4)
C11	P1	Pd1	122.8(3)	C4	C1	Pd1	107.8(3)
C11A	P1	Pd1	111.1(3)	C1	C2	Pd1	68.3(2)
C24	C23	Pd1	84.69(18)	C1	C2	C3	107.8(4)
C24	C23	C22	119.2(3)	C3	C2	Pd1	108.4(3)
C22	C23	Pd1	109.00(18)	C12	C11	P1	111.6(7)
C28	C23	Pd1	90.49(19)	C16	C11	P1	126.8(7)
C28	C23	C24	118.0(3)	C16	C11	C12	121.6(8)
C28	C23	C22	120.7(3)	C7	C6	C5	111.2(3)
C23	C24	Pd1	62.96(16)	O2	C3	C2	108.1(4)
C23	C24	C29	121.7(3)	O1	C3	O2	119.2(5)
C25	C24	Pd1	103.0(2)	O1	C3	C2	132.7(5)
C25	C24	C23	119.4(3)	C14	C15	C16	111.5(9)
C25	C24	C29	118.5(3)	C8	C7	C6	112.2(4)
C29	C24	Pd1	109.8(2)	C7	C8	C9	110.6(4)
C17	C22	C23	125.3(3)	C5	C10	C9	110.9(3)
C21	C22	C23	116.4(3)	O2	C4	C1	108.5(4)
C21	C22	C17	118.3(3)	O3	C4	O2	119.1(6)
C4	O2	C3	108.6(4)	O3	C4	C1	132.4(5)
C22	C17	P1	116.9(2)	C8	C9	C10	110.8(4)
C18	C17	P1	123.5(2)	C11	C16	C15	120.3(8)
C18	C17	C22	119.6(3)	C13	C14	C15	122.7(8)
C23	C28	C32	121.4(3)	C14	C13	C12	121.1(9)
C27	C28	C23	119.2(3)	C16A	C11A	P1	132.3(7)
C27	C28	C32	119.2(3)	C16A	C11A	C12A	114.9(7)
C26	C25	C24	122.7(3)	C12A	C11A	P1	112.7(6)
C24	C29	C30	112.5(3)	C11A	C16A	C15A	125.5(8)
C24	C29	C31	109.7(3)	C14A	C15A	C16A	109.6(8)
C30	C29	C31	110.9(3)	C13A	C14A	C15A	117.5(10)
C18	C19	C20	120.4(3)	C14A	C13A	C12A	126.6(9)
C19	C18	C17	120.6(3)	C11A	C12A	C13A	108.5(8)
C28	C32	C33	112.3(3)				

Table S47 Hydrogen Atom Coordinates ($\text{\AA} \times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 8.

Atom	x	y	z	U(eq)
H25	5921.55	6830.97	7436.95	58
H29	4493.2	7985.32	6895.42	53
H19	1851.51	8147.33	6944.43	65
H18	2403.29	7913.45	5937.01	55
H32	3177.96	5748.13	6667.74	58
H21	3351.13	6955.83	7875.4	61
H20	2305.54	7643.8	7912.23	70
H5	3225.77	8134.48	5032.49	55
H27	4835.35	4990.19	7273.23	62
H35	6545.53	5585.62	7389.85	84
H30A	6034.83	7949.63	6959.77	93
H30B	5566.57	8606.89	6712.38	93
H30C	5596.89	7895.33	6288.36	93
H12A	3623.44	5761.74	4705.4	76
H12B	3767.08	6404.02	4211.06	76
H1	5232.92	5780.18	4768.54	87
H31A	4477.94	7941.55	8040.89	105
H31B	5002.01	8576.51	7841.81	105
H31C	5327.75	7834.11	8073.66	105
H2	5759.46	5399.47	5803.84	79
H33A	3857.73	5063.88	5908.02	100
H33B	3219.89	4599.86	6207.9	100
H33C	4022.17	4491.74	6465.65	100
H34A	3597.44	4753	7662.06	113
H34B	2802.96	4816.35	7373.28	113
H34C	3135.24	5452.55	7791.94	113
H11	2944.55	6264.99	5254.29	64
H6A	4535.85	7693.84	4400.55	77
H6B	3747	7568.58	4113.6	77
H36A	6514.66	6277.95	8298.25	146
H36B	6799.75	5516.75	8522.53	146
H36C	5989.92	5743.61	8671.88	146
H15A	1673.27	5885.85	5002.98	73
H15B	1369.81	6441.5	4479.68	73
H7A	4317.04	8572.53	3598.86	92
H7B	3584.78	8797.79	3949.86	92
H8A	4466.73	9642.5	4210.45	106
H8B	4994.78	9036.32	4472.6	106
H10A	4647.3	8350.43	5542.3	80
H10B	3923.77	8568.69	5913.46	80
H9A	3660.14	9427.77	5085.84	105
H9B	4437.97	9589.19	5383.02	105
H37A	5724.66	4525.18	8000.78	199
H37B	6565.73	4480.68	7853.92	199
H37C	6005.99	4507.77	7261.18	199
H16A	2268.65	7215.35	4641.52	55
H16B	2178.84	6904.08	5360.04	55
H14A	2034.78	5284.45	4186.8	78

H14B	1886.42	5916.27	3692.77	78
H13A	2888.41	6087.68	3544.91	95
H13B	3001.5	5330.23	3867.55	95
H11A	2883.03	6799.11	4817.79	55
H16C	2201.9	6698.83	5475	84
H16D	2454.6	5917.47	5636.36	84
H15C	1475.88	5709.62	5030.04	86
H15D	1618.53	6367.69	4551.18	86
H14C	1988.37	5008.16	4337.92	109
H14D	2113.9	5658.88	3854.72	109
H13C	2997.83	5246.19	3912.01	81
H13D	2898.98	4997.2	4646.14	81
H12C	3838.92	5752.77	4742.02	74
H12D	3529.25	6296.39	4208.19	74

Table S48 Atomic Occupancy for 8.

Atom	Occupancy	Atom	Occupancy	Atom	Occupancy
C12	0.477(8)	H12A	0.477(8)	H12B	0.477(8)
C11	0.477(8)	H11	0.477(8)	C15	0.477(8)
H15A	0.477(8)	H15B	0.477(8)	C16	0.477(8)
H16A	0.477(8)	H16B	0.477(8)	C14	0.477(8)
H14A	0.477(8)	H14B	0.477(8)	C13	0.477(8)
H13A	0.477(8)	H13B	0.477(8)	C11A	0.523(8)
H11A	0.523(8)	C16A	0.523(8)	H16C	0.523(8)
H16D	0.523(8)	C15A	0.523(8)	H15C	0.523(8)
H15D	0.523(8)	C14A	0.523(8)	H14C	0.523(8)
H14D	0.523(8)	C13A	0.523(8)	H13C	0.523(8)
H13D	0.523(8)	C12A	0.523(8)	H12C	0.523(8)
H12D	0.523(8)				

Refinement model description

Number of restraints - 105, number of constraints - unknown.

Details:

1. 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

2. Restrained distances

P1-C11 ≈ P1-C11A

with sigma of 0.02

C12-C11 ≈ C12A-C11A

with sigma of 0.02

C12-C13 ≈ C12A-C13A

with sigma of 0.02

C11-C16 ≈ C11A-C16A

with sigma of 0.02

C15-C16 ≈ C15A-C16A

with sigma of 0.02

C15-C14 ≈ C15A-C14A

with sigma of 0.02

C14-C13 ≈ C14A-C13A

with sigma of 0.02

P1-C12 ≈ P1-C12A

with sigma of 0.04

P1-C16 ≈ P1-C16A

with sigma of 0.04

C12-C16 ≈ C12A-C16A

with sigma of 0.04

C12-C14 ≈ C12A-C14A

with sigma of 0.04

C11-C15 ≈ C11A-C15A

with sigma of 0.04

C11-C13 ≈ C11A-C13A

with sigma of 0.04

C15-C13 ≈ C15A-C13A

with sigma of 0.04

C16-C14 ≈ C16A-C14A

with sigma of 0.04

3. Rigid bond restraints

C11, C16, C15, C14, C13, C12

with sigma for 1-2 distances of 0.01 and sigma for 1-3 distances of 0.01

4. Uiso/Uaniso restraints and constraints

C16 ≈ C15 ≈ C14 ≈ C13 ≈ C12 ≈ C11: within 2A with sigma of

0.01 and sigma for terminal atoms of 2

Uanis(C11) ≈ Ueq, Uanis(C16) ≈ Ueq, Uanis(C15) ≈ Ueq, Uanis(C14)

≈ Ueq, Uanis(C13) ≈ Ueq, Uanis(C12) ≈ Ueq: with sigma of 0.01 and

sigma for terminal atoms of 0.02

Uanis(C14A) ≈ Ueq: with sigma of 0.001 and sigma for terminal atoms of 0.002

5. Others

Sof(C11A)=Sof(H11A)=Sof(C16A)=Sof(H16C)=Sof(H16D)=Sof(C15A)=Sof(H15C)=

Sof(H15D)=Sof(C14A)=Sof(H14C)=Sof(H14D)=Sof(C13A)=Sof(H13C)=Sof(H13D)=

Sof(C12A)=Sof(H12C)=Sof(H12D)=1-FVAR(1)

Sof(C12)=Sof(H12A)=Sof(H12B)=Sof(C11)=Sof(H11)=Sof(C15)=Sof(H15A)=Sof(H15B)=

Sof(C16)=Sof(H16A)=Sof(H16B)=Sof(C14)=Sof(H14A)=Sof(H14B)=Sof(C13)=Sof(H13A)=

Sof(H13B)=FVAR(1)

6.a Ternary CH refined with riding coordinates:

C29(H29), C32(H32), C5(H5), C35(H35), C1(H1), C2(H2), C11(H11), C11A(H11A)

6.b Secondary CH₂ refined with riding coordinates:

C12(H12A,H12B), C6(H6A,H6B), C15(H15A,H15B), C7(H7A,H7B), C8(H8A,H8B),

C10(H10A,H10B), C9(H9A,H9B), C16(H16A,H16B), C14(H14A,H14B), C13(H13A,H13B),

C16A(H16C,H16D), C15A(H15C,H15D), C14A(H14C,H14D), C13A(H13C,H13D), C12A(H12C, H12D)

6.c Aromatic/amide H refined with riding coordinates:

C25(H25), C19(H19), C18(H18), C21(H21), C20(H20), C27(H27)

6.d Idealised Me refined as rotating group:

C30(H30A,H30B,H30C), C31(H31A,H31B,H31C), C33(H33A,H33B,H33C), C34(H34A,H34B, H34C), C36(H36A,H36B,H36C), C37(H37A,H37B,H37C)

Bippyphos–Pd–MAH (12)

Single crystals of $C_{39.5}H_{46.5}Cl_2N_4O_{3.5}PPd$ [12•0.5Et2O•DCM] were selected using a MitEGen loop using paratone oil. A suitable crystal was selected and run on a Bruker APEX-II CCD diffractometer. The crystal was kept at 100.0 K during data collection. Using Olex2,¹² the structure was solved with the olex2.solve¹³ structure solution program using Charge Flipping and refined with the XL¹⁴ refinement package using Least Squares minimization.

Crystal structure determination of [12•0.5Et2O•DCM]

Crystal Data for $C_{39.5}H_{46.5}Cl_2N_4O_{3.5}PPd$ ($M = 841.57$ g/mol): monoclinic, space group $P2_1/n$ (no. 14), $a = 12.848(2)$ Å, $b = 18.223(3)$ Å, $c = 16.659(3)$ Å, $\beta = 99.686(4)^\circ$, $V = 3844.9(12)$ Å³, $Z = 4$, $T = 100.0$ K, $\mu(\text{MoK}\alpha) = 0.708$ mm⁻¹, $D_{\text{calc}} = 1.454$ g/cm³, 35443 reflections measured ($3.338^\circ \leq 2\Theta \leq 56.038^\circ$), 9241 unique ($R_{\text{int}} = 0.0341$, $R_{\text{sigma}} = 0.0344$) which were used in all calculations. The final R_1 was 0.0393 ($I > 2\sigma(I)$) and wR_2 was 0.1046 (all data).

Table S49 Crystal data and structure refinement for 12•0.5Et2O•DCM.

Identification code	12•0.5Et2O•DCM
Empirical formula	$C_{39.5}H_{46.5}Cl_2N_4O_{3.5}PPd$
Formula weight	841.57
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1/n$
$a/\text{\AA}$	12.848(2)
$b/\text{\AA}$	18.223(3)
$c/\text{\AA}$	16.659(3)
$\alpha/^\circ$	90
$\beta/^\circ$	99.686(4)
$\gamma/^\circ$	90
Volume/Å ³	3844.9(12)
Z	4
$\rho_{\text{calc}}/\text{g/cm}^3$	1.454
μ/mm^{-1}	0.708
$F(000)$	1738.0
Crystal size/mm ³	0.15 × 0.15 × 0.1
Radiation	MoK α ($\lambda = 0.71073$)
2 Θ range for data collection/°	3.338 to 56.038
Index ranges	-16 ≤ h ≤ 16, -15 ≤ k ≤ 23, -21 ≤ l ≤ 21
Reflections collected	35443
Independent reflections	9241 [$R_{\text{int}} = 0.0341$, $R_{\text{sigma}} = 0.0344$]
Data/restraints/parameters	9241/48/497
Goodness-of-fit on F^2	1.033
Final R indexes [$I >= 2\sigma(I)$]	$R_1 = 0.0393$, $wR_2 = 0.0975$
Final R indexes [all data]	$R_1 = 0.0525$, $wR_2 = 0.1046$
Largest diff. peak/hole / e Å ⁻³	1.42/-1.42

Table S50 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 12•0.5Et2O•DCM. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	$U(\text{eq})$
Pd1	4114.8(2)	7046.9(2)	3717.8(2)	13.84(7)
P1	3384.1(6)	8203.0(4)	3704.3(4)	16.36(14)
Cl2	8067.4(10)	8833.8(7)	5236.4(7)	60.3(3)
Cl1	8829.0(11)	7681.3(10)	4266.8(8)	82.0(5)
O2	3821.8(16)	5936.4(11)	5156.8(12)	21.0(4)
O3	3954.5(17)	5036.8(11)	4256.7(13)	25.1(5)
O1	4187.5(18)	6912.4(12)	5984.1(13)	27.7(5)
N4	3286.8(18)	5759.4(12)	2334.9(13)	15.4(4)
N3	4237.4(18)	6022.3(12)	2194.6(13)	15.4(4)
N1	2858.2(18)	7717.3(12)	2144.8(13)	13.8(4)
N2	2436(2)	7871.2(13)	1355.2(14)	19.2(5)
C34	5060(2)	6756.0(15)	4811.4(16)	18.4(5)
C14	2698(2)	6348.6(14)	2405.1(15)	13.9(5)
C15	1593(2)	6267.2(14)	2524.3(16)	16.1(5)
C16	797(2)	6703.4(16)	2096.2(17)	20.1(6)
C12	4288(2)	6766.4(15)	2202.4(16)	15.9(5)
C9	2767(2)	8296.1(14)	2654.4(16)	15.4(5)
C36	4248(2)	5631.7(15)	4507.7(17)	18.9(6)
C11	2086(2)	8558.5(15)	1380.1(17)	20.3(6)
C27	5048(2)	5504.2(15)	2100.8(17)	18.6(5)
C33	5017(2)	6144.6(15)	4276.2(16)	17.6(5)
C10	2268(2)	8849.1(15)	2168.6(17)	19.9(6)
C6	3866(3)	9738.1(16)	3857(2)	29.8(7)
C21	5190(2)	7198.8(16)	2024.3(18)	22.0(6)
C13	3289(2)	7004.5(14)	2336.8(15)	13.7(5)
C20	1335(2)	5731.9(17)	3053.5(19)	25.6(6)
C1	2283(2)	8312.6(17)	4302.1(17)	23.0(6)
C35	4347(2)	6594.0(16)	5389.8(17)	20.2(6)
C32	5232(2)	4923.2(16)	2640.3(19)	23.9(6)
C8	5007(3)	8917.0(17)	3164(2)	27.5(7)
C28	5614(3)	5584.9(17)	1468(2)	27.2(7)
C22	5021(3)	7711.7(19)	1398(2)	32.5(8)
C5	4362(2)	8973.3(16)	3857.3(18)	23.0(6)
C3	1490(3)	8924.8(19)	3997(2)	31.1(7)
C17	-242(2)	6602.4(18)	2197.7(19)	26.8(7)
C4	2747(3)	8438(2)	5203.4(18)	32.3(8)
C18	-491(3)	6069(2)	2718(2)	34.3(8)
C26	6203(3)	7104(2)	2468(2)	33.9(8)
C7	5115(3)	8844.3(18)	4664(2)	32.2(7)
C29	6400(3)	5081.3(19)	1393(2)	37.5(8)
C19	296(3)	5634(2)	3144(2)	36.2(8)
C30	6606(3)	4503(2)	1936(2)	38.0(8)
C2	1694(3)	7575.6(18)	4223(2)	27.9(7)
C31	6016(3)	4420.5(19)	2551(2)	32.4(7)
C25	7030(3)	7526(3)	2267(3)	53.5(13)
C37	7749(3)	8034(2)	4659(2)	41.8(9)
C24	6859(4)	8021(3)	1643(3)	63.2(16)
C23	5860(4)	8122(3)	1212(3)	57.0(14)
C3S	52(7)	4971(7)	5043(17)	37.6(14)
O1S	1133(4)	5158(3)	5179(3)	44.7(11)
C2S	1826(5)	4617(4)	5390(5)	48.8(15)
C4S	-735(5)	5615(4)	4982(5)	52.6(17)
C5S	1861(7)	3822(3)	5526(5)	72(2)
C5T	2389(7)	4927(5)	6257(4)	42(2)

Table S51 Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 12•0.5Et2O•DCM. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + 2hka^{*}b^{*}U_{12} + \dots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pd1	16.37(11)	11.98(10)	12.04(10)	-0.76(7)	-0.86(7)	1.73(7)
P1	21.2(4)	13.1(3)	13.3(3)	-3.1(3)	-1.4(3)	3.0(3)
Cl2	72.3(8)	60.1(7)	41.0(6)	12.0(5)	-12.0(5)	-10.1(6)
Cl1	58.4(8)	143.5(14)	46.5(6)	23.5(8)	15.3(6)	49.6(9)
O2	22.4(11)	21.3(10)	19.9(10)	1.2(8)	5.2(8)	0.7(8)
O3	31.1(12)	16.7(10)	25.8(11)	0.9(8)	-0.2(9)	-2.0(8)
O1	35.1(13)	30.2(12)	17.8(10)	-2.2(9)	4.8(9)	4.8(9)
N4	17.5(11)	13.2(10)	16.0(11)	0.3(8)	4.0(9)	0.7(8)
N3	16.4(11)	13.7(11)	15.6(11)	-2.7(8)	1.6(9)	1.6(8)
N1	18.7(11)	10.6(10)	11.0(10)	-0.3(8)	-1.0(8)	1.0(8)
N2	26.6(13)	16.4(11)	12.3(11)	1.6(9)	-3.1(9)	-1.1(9)
C34	18.3(13)	19.4(13)	15.3(13)	1.9(10)	-3.1(10)	0.8(10)
C14	18.1(13)	12.5(12)	10.3(12)	-0.3(9)	0.2(10)	-0.2(9)
C15	18.9(13)	13.9(12)	16.3(13)	-1.8(10)	4.9(10)	-0.5(10)
C16	21.0(14)	21.2(14)	18.0(13)	1.5(11)	3.0(11)	0.6(11)
C12	18.8(13)	14.7(12)	13.5(12)	-3.5(10)	0.3(10)	-1.6(10)
C9	18.5(13)	13.0(12)	13.7(12)	-2.5(10)	0.0(10)	0.3(10)
C36	20.6(14)	17.7(13)	16.8(13)	3.7(11)	-1.2(11)	3.8(10)
C11	27.0(15)	12.6(12)	18.2(13)	2.7(10)	-4.8(11)	-2.4(11)
C27	17.5(13)	17.0(13)	21.5(14)	-4.3(11)	3.5(11)	2.1(10)
C33	16.2(13)	18.1(13)	17.4(13)	3.0(10)	-0.6(10)	3.6(10)
C10	24.5(15)	13.3(12)	20.2(14)	0.9(11)	-1.4(11)	0.7(11)
C6	37.5(19)	16.6(14)	32.6(17)	-6.3(12)	-1.9(14)	-0.2(12)
C21	19.6(14)	23.2(14)	25.1(15)	-14.0(12)	9.0(11)	-7.2(11)
C13	15.5(12)	11.8(11)	12.6(12)	-1.5(9)	-1.0(9)	1.0(10)
C20	24.4(16)	23.9(15)	29.7(16)	7.5(12)	8.4(12)	3.1(12)
C1	28.8(16)	24.3(15)	15.9(13)	-2.0(11)	3.5(11)	8.6(12)
C35	22.4(14)	20.2(13)	15.8(13)	3.0(11)	-3.1(11)	4.6(11)
C32	23.8(15)	23.8(15)	24.6(15)	-0.4(12)	5.5(12)	5.4(12)
C8	25.9(16)	20.5(15)	34.7(17)	-6.2(13)	1.6(13)	-5.8(12)
C28	35.0(18)	18.6(14)	30.8(16)	-2.2(12)	13.3(14)	3.6(12)
C22	40.3(19)	35.3(17)	24.2(16)	-6.8(14)	12.4(14)	-21.3(15)
C5	28.0(16)	16.1(13)	23.1(15)	-6.6(11)	-1.4(12)	-0.3(11)
C3	32.8(18)	32.6(17)	28.9(17)	0.4(14)	8.8(14)	14.5(14)
C17	19.5(15)	36.5(17)	24.9(15)	2.8(13)	4.9(12)	5.4(13)
C4	44(2)	35.2(18)	17.0(15)	-4.9(13)	4.5(14)	11.6(15)
C18	20.1(16)	46(2)	40.0(19)	6.8(16)	15.2(14)	0.5(14)
C26	18.7(15)	40.6(19)	43(2)	-22.4(16)	7.8(14)	0.4(13)
C7	35.6(18)	25.8(16)	29.4(17)	-7.4(13)	-11.4(14)	0.5(14)
C29	42(2)	29.8(17)	48(2)	-2.5(16)	27.5(17)	7.2(15)
C19	31.4(18)	38.9(19)	42(2)	15.3(16)	18.0(16)	-1.1(15)
C30	33.3(19)	31.4(18)	53(2)	0.8(16)	19.6(17)	14.5(15)
C2	29.5(17)	30.3(17)	25.8(16)	-0.1(13)	9.8(13)	3.3(13)
C31	33.0(18)	28.1(16)	37.2(18)	4.6(14)	9.0(15)	14.4(14)
C25	22.0(18)	75(3)	67(3)	-51(3)	19.2(18)	-18.6(18)
C37	33(2)	61(3)	30.7(18)	9.1(17)	3.5(15)	2.8(17)
C24	57(3)	81(3)	63(3)	-43(3)	43(2)	-53(3)
C23	76(3)	61(3)	42(2)	-20(2)	34(2)	-50(2)
C3S	41(2)	33(3)	41(4)	10(2)	12(2)	-8(2)
O1S	45(2)	38(2)	53(3)	4(2)	14(2)	4.3(19)
C2S	40(3)	54(3)	59(3)	13(3)	26(3)	0(3)
C4S	49(4)	50(4)	53(4)	22(3)	-7(3)	-14(3)
C5S	100(6)	53(3)	81(5)	-20(4)	69(4)	-23(4)
C5T	51(5)	42(5)	42(4)	3(4)	34(4)	-16(4)

Table S52 Bond Lengths for 12•0.5Et₂O•DCM.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pd1	P1	2.3051(8)	C9	C10	1.381(4)
Pd1	C34	2.081(3)	C36	C33	1.458(4)
Pd1	C12	2.622(3)	C11	C10	1.399(4)
Pd1	C33	2.133(3)	C27	C32	1.383(4)
Pd1	C13	2.367(3)	C27	C28	1.385(4)
P1	C9	1.803(3)	C6	C5	1.533(4)
P1	C1	1.873(3)	C21	C22	1.390(5)
P1	C5	1.873(3)	C21	C26	1.396(4)
Cl2	C37	1.757(4)	C20	C19	1.380(5)
Cl1	C37	1.752(4)	C1	C3	1.538(4)
O2	C36	1.406(3)	C1	C4	1.537(4)
O2	C35	1.398(3)	C1	C2	1.536(4)
O3	C36	1.200(3)	C32	C31	1.388(4)
O1	C35	1.195(4)	C8	C5	1.534(4)
N4	N3	1.368(3)	C28	C29	1.386(4)
N4	C14	1.330(3)	C22	C23	1.389(5)
N3	C12	1.358(3)	C5	C7	1.536(4)
N3	C27	1.434(3)	C17	C18	1.375(5)
N1	N2	1.365(3)	C18	C19	1.383(5)
N1	C9	1.371(3)	C26	C25	1.398(5)
N1	C13	1.427(3)	C29	C30	1.385(5)
N2	C11	1.334(4)	C30	C31	1.381(5)
C34	C33	1.422(4)	C25	C24	1.366(7)
C34	C35	1.467(4)	C24	C23	1.374(7)
C14	C15	1.474(4)	C3S	O1S	1.411(9)
C14	C13	1.431(4)	C3S	C4S	1.541(9)
C15	C16	1.393(4)	O1S	C2S	1.336(6)
C15	C20	1.392(4)	C2S	C5S	1.467(7)
C16	C17	1.387(4)	C2S	C5T	1.606(8)
C12	C21	1.472(4)	C4S	C5S ¹	1.858(11)
C12	C13	1.409(4)			

Table S52 footnotes: ¹-X,1-Y,1-Z**Table S53 Bond Angles for 12•0.5Et₂O•DCM.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
P1	Pd1	C12	105.63(6)	C9	C10	C11	105.2(2)
P1	Pd1	C13	84.55(6)	C22	C21	C12	118.9(3)
C34	Pd1	P1	114.71(8)	C22	C21	C26	119.7(3)
C34	Pd1	C12	131.42(10)	C26	C21	C12	121.5(3)
C34	Pd1	C33	39.43(11)	N1	C13	Pd1	106.36(16)
C34	Pd1	C13	160.51(10)	N1	C13	C14	126.0(2)
C33	Pd1	P1	154.07(8)	C14	C13	Pd1	96.15(16)
C33	Pd1	C12	98.15(10)	C12	C13	Pd1	83.86(15)
C33	Pd1	C13	121.37(10)	C12	C13	N1	125.1(2)
C13	Pd1	C12	32.29(9)	C12	C13	C14	105.4(2)

C9	P1	Pd1	101.97(9)	C19	C20	C15	119.8(3)
C9	P1	C1	104.93(13)	C3	C1	P1	114.8(2)
C9	P1	C5	103.70(13)	C4	C1	P1	109.4(2)
C1	P1	Pd1	115.80(10)	C4	C1	C3	110.0(2)
C5	P1	Pd1	114.89(10)	C2	C1	P1	105.42(19)
C5	P1	C1	113.42(14)	C2	C1	C3	108.5(3)
C35	O2	C36	108.6(2)	C2	C1	C4	108.6(3)
C14	N4	N3	105.7(2)	O2	C35	C34	108.4(2)
N4	N3	C27	118.3(2)	O1	C35	O2	120.3(3)
C12	N3	N4	113.0(2)	O1	C35	C34	131.3(3)
C12	N3	C27	128.6(2)	C27	C32	C31	118.9(3)
N2	N1	C9	112.2(2)	C27	C28	C29	118.8(3)
N2	N1	C13	118.6(2)	C23	C22	C21	120.0(4)
C9	N1	C13	129.2(2)	C6	C5	P1	114.3(2)
C11	N2	N1	104.1(2)	C6	C5	C8	109.7(3)
C33	C34	Pd1	72.25(15)	C6	C5	C7	109.9(2)
C33	C34	C35	106.9(2)	C8	C5	P1	106.39(19)
C35	C34	Pd1	106.81(18)	C8	C5	C7	108.0(3)
N4	C14	C15	120.4(2)	C7	C5	P1	108.3(2)
N4	C14	C13	110.5(2)	C18	C17	C16	120.1(3)
C13	C14	C15	129.1(2)	C17	C18	C19	120.1(3)
C16	C15	C14	120.9(2)	C21	C26	C25	118.9(4)
C20	C15	C14	119.6(2)	C30	C29	C28	120.5(3)
C20	C15	C16	119.5(3)	C20	C19	C18	120.5(3)
C17	C16	C15	120.0(3)	C31	C30	C29	119.9(3)
N3	C12	Pd1	101.08(17)	C30	C31	C32	120.5(3)
N3	C12	C21	124.8(2)	C24	C25	C26	121.0(4)
N3	C12	C13	105.4(2)	Cl1	C37	Cl2	112.5(2)
C21	C12	Pd1	106.67(17)	C25	C24	C23	120.2(4)
C13	C12	Pd1	63.85(14)	C24	C23	C22	120.2(4)
C13	C12	C21	129.5(3)	O1S	C3S	C4S	116.3(9)
N1	C9	P1	117.31(19)	C2S	O1S	C3S	117.3(7)
N1	C9	C10	106.1(2)	O1S	C2S	C5S	140.5(7)
C10	C9	P1	136.2(2)	O1S	C2S	C5T	99.0(6)
O2	C36	C33	108.6(2)	C3S ¹	C4S	C3S	6(2)
O3	C36	O2	119.0(3)	C3S ¹	C4S	O1S ¹	58.2(6)
O3	C36	C33	132.4(3)	C3S ¹	C4S	C2S ¹	108.9(9)
N2	C11	C10	112.4(2)	C3S	C4S	C5S ¹	154.5(11)
C32	C27	N3	118.7(3)	C3S ¹	C4S	C5S ¹	149.3(13)
C32	C27	C28	121.4(3)	O1S ¹	C4S	C3S	59.9(6)
C28	C27	N3	119.8(3)	O1S ¹	C4S	C5S ¹	102.7(5)
C34	C33	Pd1	68.33(15)	C2S ¹	C4S	C3S	111.8(7)
C34	C33	C36	107.1(2)	C2S ¹	C4S	O1S ¹	52.8(4)
C36	C33	Pd1	105.51(18)	C2S ¹	C4S	C5S ¹	50.5(4)

Table S53 footnotes: ¹-X,1-Y,1-Z

Table S54 Hydrogen Atom Coordinates ($\text{\AA} \times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 12•0.5Et₂O•DCM.

Atom	x	y	z	U(eq)
H34	5744.26	7015.14	4997.79	22
H16	967.26	7070.48	1734.39	24
H11	1751.98	8821.15	914.82	24
H33	5660.28	5967.58	4070.95	21
H10	2086.21	9324.46	2334.17	24
H6A	3355.05	9805.42	3355.14	45
H6B	4420.13	10111.67	3886.97	45
H6C	3506.38	9786.17	4328.29	45
H20	1872.77	5434.44	3351.68	31
H32	4828.59	4869.11	3065.05	29
H8A	5294.01	8419.94	3149.4	41
H8B	5587.56	9271.9	3254.26	41
H8C	4549.67	9023.18	2643.98	41
H28	5466.24	5978.49	1092.51	33
H22	4331.35	7781.74	1097.79	39
H3A	1863.45	9394.69	4007.77	47
H3B	954.8	8953.69	4351.27	47
H3C	1148.03	8816.18	3438.99	47
H17	-783.57	6901.81	1907.15	32
H4A	3294.53	8070.42	5380.47	48
H4B	2186.15	8393.76	5532.72	48
H4C	3057.54	8930.07	5271.93	48
H18	-1203.83	5999.88	2785.36	41
H26	6328.71	6757.31	2900.01	41
H7A	4720.74	8879.45	5117.34	48
H7B	5674.15	9216.01	4729.28	48
H7C	5430.67	8354.99	4659.56	48
H29	6800.69	5133.1	966.3	45
H19	119.6	5265.79	3501.61	43
H30	7152.85	4163.67	1885.55	46
H2A	1405.4	7483.97	3648.78	42
H2B	1117.35	7591.81	4539.3	42
H2C	2185.12	7180.88	4429.32	42
H31	6147.43	4016.87	2914.44	39
H25	7721.46	7468.04	2569.4	64
H37A	7489.76	7656.45	5004.67	50
H37B	7170.76	8144.25	4202.19	50
H24	7433.01	8296.36	1507.25	76
H23	5742.18	8473.16	785.28	68
H3SA	-79.86	4645.31	5491.54	45
H3SB	-100.75	4684.01	4532.24	45
H2SA	2232.04	4803.23	5907.74	59
H2SB	2307.21	4676.55	4988.28	59
H2SC	2327.98	4568	5002.37	59
H2SD	1472.35	4140.92	5441.27	59
H4SC	-575.72	6001.04	4611.92	79
H4SA	-646.3	5808.54	5538.51	79
H4SB	-1464.18	5448.58	4815	79
H5SC	1649.98	3712.1	6051.48	108
H5SA	2580.54	3642.66	5526.81	108
H5SB	1375.71	3578.44	5089.6	108
H5TA	2170.82	5436.05	6318.58	63
H5TB	3157.47	4906.61	6289.3	63
H5TC	2183.45	4626.63	6692.72	63

Table S55 Atomic Occupancy for 12•0.5Et2O•DCM.

Atom	Occupancy	Atom	Occupancy	Atom	Occupancy
C3S	0.5	H3SA	0.5	H3SB	0.5
O1S	0.5	C2S	0.5	H2SA	0.615(8)
H2SB	0.615(8)	H2SC	0.385(8)	H2SD	0.385(8)
C4S	0.5	H4SC	0.5	H4SA	0.5
H4SB	0.5	C5S	0.615(8)	H5SC	0.615(8)
H5SA	0.615(8)	H5SB	0.615(8)	C5T	0.385(8)
H5TA	0.385(8)	H5TB	0.385(8)	H5TC	0.385(8)

Refinement model description

Number of restraints - 48, 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

C4S-C3S = C5S-C2S = C2S-C5T

1.54 with sigma of 0.01

O1S-C3S = O1S-C2S

1.45 with sigma of 0.01

C4S-O1S

2.44 with sigma of 0.01

O1S-C5S

2.44 with sigma of 0.01

O1S-C5T

2.44 with sigma of 0.01

C3S-C2S

2.29 with sigma of 0.01

3. Rigid bond restraints

C4S, C3S, O1S, C2S, C5S, C5T

with sigma for 1-2 distances of 0.005 and sigma for 1-3 distances of 0.01

4. Uiso/Uaniso restraints and constraints

C4S ≈ C3S ≈ O1S ≈ C2S ≈ C5S ≈ C5T: within 2A with sigma of

0.005 and sigma for terminal atoms of 0.01

5. Others

Sof(H2SD)=Sof(H2SC)=Sof(C5T)=Sof(H5TA)=Sof(H5TB)=Sof(H5TC)=1-FVAR(1)

Sof(H2SA)=Sof(H2SB)=Sof(C5S)=Sof(H5SA)=Sof(H5SB)=Sof(H5SC)=FVAR(1)

Fixed Sof: C3S(0.5) H3SA(0.5) H3SB(0.5) O1S(0.5) C2S(0.5) C4S(0.5) H4SA(0.5)

H4SC(0.5) H4SB(0.5)

6.a Ternary CH refined with riding coordinates:

C34(H34), C33(H33)

6.b Secondary CH2 refined with riding coordinates:

C37(H37A,H37B), C3S(H3SA,H3SB), C2S(H2SA,H2SB), C2S(H2SD,H2SC)

6.c Aromatic/amide H refined with riding coordinates:

C16(H16), C11(H11), C10(H10), C20(H20), C32(H32), C28(H28), C22(H22),

C17(H17), C18(H18), C26(H26), C29(H29), C19(H19), C30(H30), C31(H31), C25(H25),

C24(H24), C23(H23)

6.d Idealised Me refined as rotating group:

C6(H6A,H6B,H6C), C8(H8A,H8B,H8C), C3(H3A,H3B,H3C), C4(H4A,H4B,H4C), C7(H7A, H7B,H7C), C2(H2A,H2B,H2C), C4S(H4SA,H4SC,H4SB), C5S(H5SA,H5SB,H5SC), C5T(H5TA, H5TB,H5TC)

VI: References

- (1) Zalesskiy, S. S.; Ananikov, V. P. $\text{Pd}_2(\text{dba})_3$ as a Precursor of Soluble Metal Complexes and Nanoparticles: Determination of Palladium Active Species for Catalysis and Synthesis. *Organometallics* **2012**, *31*, 2302–2309.
- (2) Zheng, J.; Yao, Y.; Li, M.; Wang, L.; Zhang, X. A Non-MPD-Type Reverse Osmosis Membrane with Enhanced Permselectivity for Brackish Water Desalination. *J. Membrane Sci.* **2018**, *565*, 104–111.
- (3) Cavell, K. J.; Stufkens, D. J.; Vrieze, K. 1,4-Diazabutadiene Olefin Complexes of Zerovalent Palladium: Preparation and Characterization. *Inorg. Chim. Acta* **1981**, *47*, 67–76.
- (4) Lee, J.-Y.; Shen, J.-S.; Tzeng, R.-J.; Lu, I.-C.; Lii, J.-H.; Hu, C.-H.; Lee, H. M. Well-Defined Palladium(0) Complexes Bearing N-Heterocyclic Carbene and Phosphine Moieties: Efficient Catalytic Applications in the Mizoroki–Heck Reaction and Direct C–H Functionalization. *Dalton Trans.* **2016**, *45*, 10375–10388.
- (5) Wang, D.; Zheng, Y.; Yang, M.; Zhang, F.; Mao, F.; Yu, J.; Xia, X. Room-Temperature Cu-Catalyzed N-Arylation of Aliphatic Amines in Neat Water. *Org. Biomol. Chem.* **2017**, *15*, 8009–8012.
- (6) DeAngelis, A. J.; Gildner, P. G.; Chow, R.; Colacot, T. J. Generating Active “L-Pd(0)” via Neutral or Cationic π -Allylpalladium Complexes Featuring Biaryl/Bipyrazolylphosphines: Synthetic, Mechanistic, and Structure–Activity Studies in Challenging Cross-Coupling Reactions. *J. Org. Chem.* **2015**, *80*, 6794–6813.
- (7) Jiang, Y.; Wang, Q.-Q.; Liang, S.; Hu, L.-M.; Little, R. D.; Zeng, C.-C. Electrochemical Oxidative Amination of Sodium Sulfinates: Synthesis of Sulfonamides Mediated by NH_4I as a Redox Catalyst. *J. Org. Chem.* **2016**, *81*, 4713–4719.
- (8) Ueda, S.; Su, M.; Buchwald, S. L. Completely N1-Selective Palladium-Catalyzed Arylation of Unsymmetric Imidazoles: Application to the Synthesis of Nilotinib. *J. Am. Chem. Soc.* **2012**, *134*, 700–706.
- (9) Littke, A. F.; Fu, G. C. A Versatile Catalyst for Heck Reactions of Aryl Chlorides and Aryl Bromides under Mild Conditions. *J. Am. Chem. Soc.* **2001**, *123*, 6989–7000.
- (10) Gowrisankar, S.; Sergeev, A. G.; Anbarasan, P.; Spannenberg, A.; Neumann, H.; Beller, M. A General and Efficient Catalyst for Palladium-Catalyzed C–O Coupling Reactions of Aryl Halides with Primary Alcohols. *J. Am. Chem. Soc.* **2010**, *132*, 11592–11598.
- (11) Abate, A.; Hollman, D. J.; Teuscher, J.; Pathak, S.; Avolio, R.; D’Errico, G.; Vitiello, G.; Fantacci, S.; Snaith, H. J. Protic Ionic Liquids as P-Dopant for Organic Hole Transporting Materials and Their Application in High Efficiency Hybrid Solar Cells. *J. Am. Chem. Soc.* **2013**, *135*, 13538–13548.
- (12) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. a. K.; Puschmann, H. OLEX2: A Complete Structure Solution, Refinement and Analysis Program. *J Appl. Cryst.* **2009**, *42*, 339–341.
- (13) Bourhis, L. J.; Dolomanov, O. V.; Gildea, R. J.; Howard, J. a. K.; Puschmann, H. The Anatomy of a Comprehensive Constrained, Restrained Refinement Program for the Modern Computing Environment – Olex2 Dissected. *Acta Cryst. A* **2015**, *71*, 59–75.
- (14) Sheldrick, G. M. A Short History of SHELX. *Acta Cryst. A* **2008**, *64*, 112–122.