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Acrylate formation from CO_2 and ethylene: Catalysis with palladium and mechanistic insight

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Supporting Information

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I. General Considerations

All air- and moisture-sensitive manipulations were carried out using standard vacuum line, Schlenk, and cannula techniques or in an MBraun inert atmosphere dry box containing an atmosphere of purified argon. Solvents for air- and moisture-sensitive manipulations were dried with a MBraun SPS 800 solvent purification system, degassed, and stored over molecular sieves, or dried and deoxygenated using literature procedures.[1] (η^5-Cp)Pd(η^3-allyl),[2] 1,2-bis(di-*tert*-butylphosphino)ethane,[3,4] and sodium 2-fluorophenolate[5] were prepared according to literature procedures. All other reagents were purchased from Sigma Aldrich. Gases were purchased from Air Liquide.

^{1}H, ^{31}P, and ^{13}C NMR spectra were recorded on Bruker Advance 200, 400, 500, or 600 MHz spectrometers. All ^{1}H and ^{13}C NMR chemical shifts are reported in ppm relative to $SiMe_4$ using the ^{1}H (residual) and ^{13}C chemical shifts of the solvent as a secondary standard. ^{31}P NMR was referenced to triphenylphosphine. Elemental analyses and mass spectra were recorded by the analytical service of the chemistry department of the University of Heidelberg. Mass spectra were recorded on a Finnigan LCQ with a quadrupole ion trap (positive ion channel).

Single crystals suitable for X-ray diffraction were coated with a perfluorinated polyether oil in a drybox, transferred to a nylon loop or micro mount and then quickly transferred to the goniometer head in a nitrogen stream at 200(2) K. Data collection was performed with Mo-Kα radiation (λ = 0.71073 Å) from a Incoatec IμS microsource on a Bruker APEX-II diffractometer. A complete sphere in reciprocal space was covered by 0.5° ω-scans in all cases. Intensities were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied using SADABS[6] based on the Laue symmetry of the reciprocal space. The structure was solved by direct methods and refined against F^2 with a Full-matrix least-squares algorithm using the SHELXTL software package.[7] Hydrogen atoms were treated using appropriate riding models, unless otherwise noted for the particular structures. CCDC 1050643 (**2**), CCDC 1050644 (**3**), CCDC 1050645 (**5**) and CCDC 1050646 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

II. Preparation and Characterization of Compounds

Preparation of (d^{t}bpe)Pd(η^2-CH_2=CH_2) (**1**). (η^5-Cp)Pd(η^3-allyl) (21.3 mg, 0.1 mol) and 1,2-bis(di-*tert*-butylphosphino)ethane (38.2 mg, 0.1 mmol) were dissolved in THF-d_8 and transferred to a high-pressure NMR tube. The tube was charged with ethylene (8 bar) and heated to 45 °C for 2 h. Aftrer removing the solvent *in vacuo*, the prectipitate was washed with cold pentane (1 mL, –20 °C) and the product was dried *in vacuo* to yield 28 mg (55%). ^{1}H NMR (600 MHz, C_6D_6): δ 1.23 – 1.15 (m, 36H, (CH_3)$_3$CP), 1.83 – 1.76 (m, 4H, PCH_2), 2.85 (dd, J_{HH} = 1.5, 2.7 Hz, 1H, CHH=CH*H*), 2.92 (dd, J_{HH} = 2.9, 1.4 Hz, 1H, CHH=C*H*H), 3.09 (dd, J_{HH} = 6.6, 1.4 Hz, 1H, C*H*H=CHH), 3.14 (dd, J_{HH} = 6.8, 1.0 Hz, 1H, CH*H*=CHH). ^{13}C{^{1}H} NMR (600 MHz, C_6D_6): δ = 38.6 (t, $^2J_{PC}$ = 10.1 Hz, *C*HH=*C*HH), 33.7 (t, (CH_3)$_3$*C*P, $^1J_{PC}$ = 2.8 Hz), 29.7 (d, (*C*H_3)$_3$CP, $^2J_{PC}$ = 4.8 Hz), 23.8 (t, P*C*H_2, $^1J_{PC}$ = 15.0). ^{31}P NMR (81 MHz, THF-d_8): δ = 84.0 (s). Elemental analysis calcd. for $C_{24}H_{52}OPdP_2$: C 54.90, H 9.98. Found C 54.48, 9.83.

Preparation of (d^{t}bpe)Pd(η^2-CH_2CHCO_2H) (**2**). A 60 mL steel autoclave was charged with (η^5-Cp)Pd(η^3-allyl) (400 mg, 1.88 mmol), 1,2-bis(di-*tert*-butylphosphino)ethane (626 mg, 1.88 mmol) and THF (40 mL) in the glovebox. The autoclave was removed from the glovebox and charged with ethylene (30 bar) at 17 °C for 2 h, after which the pressure was released and the crude reaction mixture was transferred to a Schlenk tube in a glovebox. The reaction mixture was cooled to 0 °C followed by addition of acrylic acid (160 μL, 2.30 mmol) and stirred for 16 h. The solvent was removed *in vacuo* and the resulting solid was washed with pentane to afford 711 mg (76%)

of **2** as a yellow powder. ^{1}H NMR (600 MHz, C_6D_6): δ 1.19 – 0.95 (m, 36H, (C*H*$_3$)$_3$CP), 1.39 – 1.33 (m, 4H, PC*H*$_2$), 2.93 – 2.89 (m, 1H, CH*H*=CHCO$_2$H), 3.48 – 3.44 (m, 1H, C*H*H=CHCO$_2$H), 3.99 – 3.94 (m, 1H, CHH=C*H*CO$_2$H), 13.57 (s, 1H, CHH=CHCO$_2$*H*). ^{13}C{^{1}H} NMR (151 MHz, C_6D_6): δ 181.3 (s, CHH=CH*C*O$_2$H), 49.3 (dd, $^{2}J_{PC}$ = 18.8, 5.4 Hz, CHH=*C*HCO$_2$H), 40.0 (d, $^{2}J_{PC}$ = 33 Hz, *C*HH=CHCO$_2$H), 35.2 – 33.9 (m, (CH$_3$)$_3$*C*P), 30.3 – 29.9 (m, (*C*H$_3$)$_3$CP), 24.1 – 23.3 (m, P*C*H$_2$). ^{31}P{^{1}H} NMR (243 MHz, C_6D_6): δ 89.3 (d, $^{3}J_{PP}$ = 32 Hz), 81.1 (d, $^{3}J_{PP}$ = 32 Hz). IR (KBr): ν_{CO} = 1634 cm^{-1}. Elemental analysis calcd. for $C_{21}H_{44}O_2PdP_2$: C 50.76, H 8.92. Found C 50.82, H 8.90.

Preparation of (dcpe)Pd(CH$_2$CH$_3$)$_2$ (**3**).[8] A 20 mL scintillation vial was charged with 1,2-bis(diphenylphosphino)ethane (376 mg, 490 μmol), Pd(OAc)$_2$ (200 mg, 490 μmol), THF (*ca*. 5 mL) and a stirring bar. The mixture was stirred for *ca*. 15 min, over which time the colour changed from cloudy white to clear green. Meanwhile, a second 20 mL scintillation vial was charged with THF (*ca*. 5 mL) and Et$_3$Al (132 μL, 562 μmol) and the solution was added dropwise with a Pasteur pipette to the first solution. A quick color change to yellow, followed by orange, bright pink and red was observed. The reaction was stirred for 1 h and the solvent was removed *in vacuo*. The pink-white solid was taken into a minimal amount of THF. Recrystallization at –35 °C and washing with cold pentane yielded 140 mg (50%) of **3** in two crops as white crystals suitable for X-ray characterization. ^{31}P NMR (THF-d_8, 20 °C): δ 52.61. Elemental analysis calcd. for $C_{30}H_{58}P_2Pd$: C 61.37, H 9.96. Found: C 61.04, H 10.17.

In situ preparation of (dcpe)Pd(η^2-H$_2$C=CH$_2$).[8,9] A J-Young NMR tube was charged with **3** (25.0 mg, 42.5 μmol) and THF-d_8 (*ca*. 1 mL) and heated to 70 °C for 2 h. This resulted in compete conversion of **3** to (dcpe)Pd(η^2-H$_2$C=CH$_2$), as observed by ^{31}P-NMR when compared with the data from literature given for this compound. ^{31}P NMR (THF-d_8, 20 °C): δ 51.95.

Preparation of (dcpe)Pd(η^2-CH$_2$CHCO$_2$H) (**4**). A 20 mL scintillation vial was charged with (η^5-Cp)Pd(η^3-allyl) (50.0 mg, 235 μmol), 1,2-bis(dicyclohexylphosphino)ethane (99 mg, 235 μmol), and a magnetic stirring bar and chilled to –35 °C for 20 min. The solids were stirred and cool THF (5 mL, –35 °C) was added, upon which the colour turned immediately to peach. The mixture was stirred for *ca.* 5 min. and acrylic acid (17 mg, 235 μmol) was added. The mixture was stirred for *ca.* 1 h and a pale yellow solution was observed. The solvent was reduced *in vacuo* to *ca.* 5 mL. Crystallization at –35 °C for 3 d and washing with THF at –35 °C yielded 42 mg (30%) of **4** as a white crystalline solid. ^{1}H NMR (600.13 MHz, THF-d_8, 20 °C): δ 1.23 (20 H, *cy*), 1.73 (20 H, *cy*), 1.99 (2H, PC*H*$_2$CH$_2$P), 2.35 (m, 1H, C*H*$_2$CHCO$_2$H), 2.72 (m, 1H, C*H*$_2$CHCO$_2$H), 3.34 (dtd, $^{3}J_{HH}$ = 11.8 Hz, $^{3}J_{HH}$ = 8.6 Hz, $^{3}J_{HP}$ = 3.3 Hz, 1H, CH$_2$C*H*CO$_2$H), 9.95 (1H, CH$_2$CHCO$_2$*H*), *cy*-C*H* not located. ^{13}C{^{1}H} NMR (151 MHz, THF-d_8, 20 °C): δ 22.3 (t, average of $^{1}J_{CP}$ and $^{2}J_{CP}$ = 17.7 Hz, P*C*H$_2$CH$_2$P), 23.2 (t, average of $^{1}J_{CP}$ and $^{2}J_{CP}$ = 18.9 Hz, PCH$_2$*C*H$_2$P), 26.7 – 30.7 (m. *cy*), 35.5 – 35.8 (m, *cy*-C*H*) 37.9 (d, $^{2}J_{CP}$ = 31.5 Hz, *C*H$_2$CHCO$_2$H), 48.4 (dd, $^{1}J_{CP}$ = 20.5 Hz, $^{2}J_{CP}$ = 5.5 Hz, CH$_2$*C*HCO$_2$H), 177.2 (CH$_2$CH*C*O$_2$H). ^{31}P{^{1}H} NMR (81 MHz, THF-d_8, 20 °C): δ 52.7 (d, $^{3}J_{PP}$ = 30.0 Hz, *P*CH$_2$CH$_2$P), 61.26 (d, $^{3}J_{PP}$ = 30.0 Hz, PCH$_2$CH$_2$*P*). IR (KBr): ν_{CO} = 1629.5 cm^{-1}. Elemental analysis calcd. for $C_{33}H_{60}O_3P_2Pd$·THF: C 58.88, H 8.98. Found: C 58.80, H 8.79.

Preparation of a mixture of (dcpe)Pd(η^2-CH$_2$CHCO$_2$H) (**4**) *and (dcpe)Pd(-CH$_2$CHCO$_2$-)* (**5**). A solution of **3** (20 mg, 341 μmol) in THF-d_8 was filtered through a pipette with celite into a J-Young NMR tube. Acrylic acid (2.3 μL, 341 μmol) was added, and the tube was heated to 70 °C for 2 h, after which no more starting material was left. **5** was crystallized from this mixture at –35 °C. ^{13}C{^{1}H} NMR (151 MHz, THF-d_8, 20 °C): δ 18.4 (dd, $^{1}J_{CP}$ = 20.3 Hz, $^{2}J_{CP}$ = 9.0 Hz, P*C*H$_2$CH$_2$P), 26.7 – 30.0 (m, *cy*), 34.6 – 35.9 (m, *cy*-C*H*), 38.6 (d, $^{3}J_{CP}$ = 6.3 Hz, -CH$_2$*C*H$_2$CO$_2$-), 189.2 (d, $^{3}J_{CP}$

= 11.5 Hz, -$CH_2CH_2CO_2$-), not all assignments could be made due to overlapping regions with **4**. The ratio between **4** and **5** is *ca*. 1:1 by integration of the corresponding signals in ^{31}P NMR. ^{31}P{^{1}H} NMR (243 MHz, THF-d_8, 20 °C): δ 57.5 (d, $^3J_{PP}$ = 20.1 Hz, *P*CH_2CH_2P), 66.8 (d, $^3J_{PP}$ = 20.1 Hz, PCH_2CH_2*P*).

Ligand screening for one-pot synthesis of sodium acrylate. A 60 mL steel autoclave was charged with (η^5-Cp)Pd(η^3-allyl) (34 mg, 160 μmol), ligand (160 μmol, see Figure S1) and THF (20 mL) in an argon glovebox. The autoclave was removed from the glovebox, charged with ethylene (30 bar) and stirred at 17 °C for 1 h under active ethylene pressure. The ethylene pressure was released and the autoclave transferred to the glovebox to add sodium 2-fluorophenolate (371 mg, 3.20 mmol). The autoclave was removed from the glovebox, charged with ethylene (5 bar) and CO_2 (10 bar), and stirred at 120 °C for 20 h. After pressure release the crude reaction mixture was transferred to a 100 mL glass bottle with D_2O (15 mL). Tetramethylammonium iodide (25.1 g, 130 μmol) were dissolved in D_2O (5 mL) and added to the glass bottle as an internal standard. The vial was rinsed with D_2O (5 mL). Et_2O (30 mL) was added to the aqueous phase, shaken, and the layers allowed to separate. The aqueous phase (2 mL) was partially removed with a syringe, centrifuged to separate residual precipitate, and the liquid transferred to a glass NMR tube for analysis. The TON was determined by ^{1}H NMR (200 MHz, 70 scans) according to the ratio of sodium acrylate to the standard, tetramethylammonium iodide.

Figure S1. Ligands used in screening experiments.

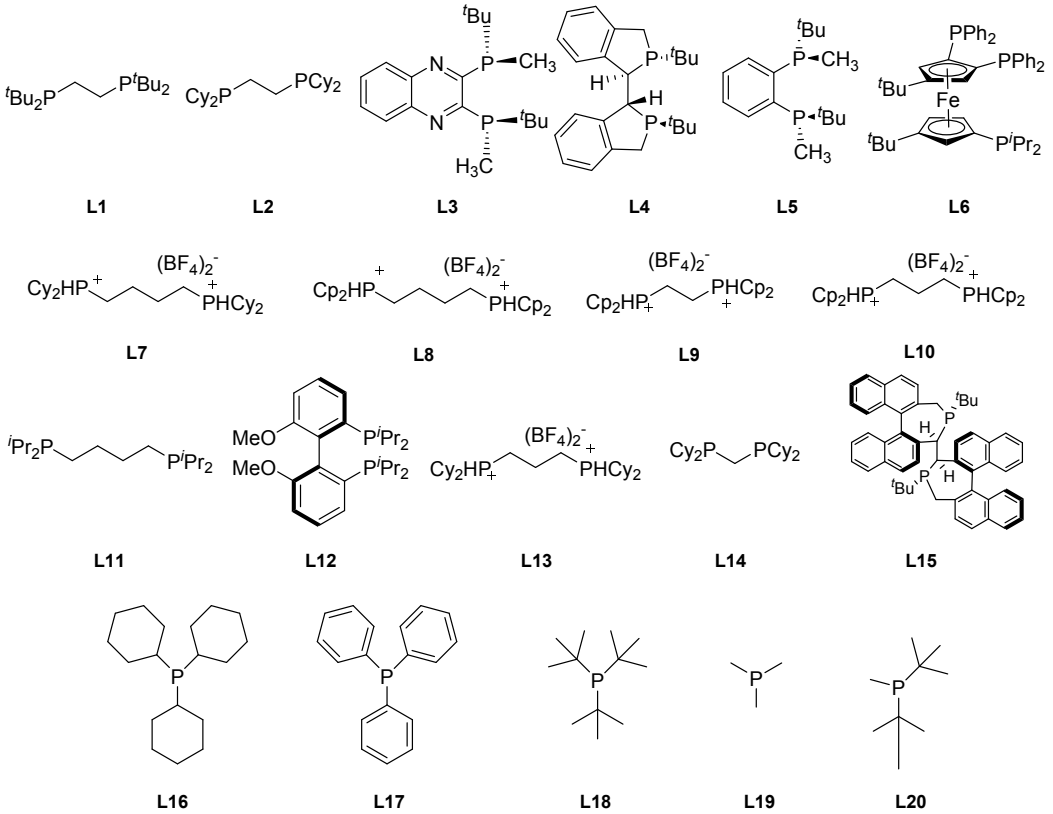

Table S1. Results from ligand screening with 2-fluorosodiumphenolate as base, 120 °C, 20 h. Tetramethylammonium iodide used as internal standard.

[Pd] precursor	mmol [Pd]	ligand	mmol ligand	mmol base	p_{C2H4} (bar)	p_{CO2} (bar)	TON
(η^5-Cp)Pd(η^3-allyl)	0.2	L1	0.22	10	5	10	1.8(3)[a]
(η^5-Cp)Pd(η^3-allyl)	0.2	L2	0.22	10	5	10	19(7)[b]

(COD)$PdCl_2$[c]	0.2	L2	0.22	10	5	10	15
(η^5-Cp)Pd(η^3-allyl)	0.2	L3	0.22	10	5	10	0.6
(η^5-Cp)Pd(η^3-allyl)	0.2	L4	0.22	10	5	10	2.3
(η^5-Cp)Pd(η^3-allyl)	0.2	L5	0.22	10	5	10	3.3
(η^5-Cp)Pd(η^3-allyl)	0.2	L6	0.22	10	5	10	0.5
(η^5-Cp)Pd(η^3-allyl)	0.2	L7	0.22	10	5	10	2.01
(η^5-Cp)Pd(η^3-allyl)	0.2	L8	0.22	10	5	10	2.8
(η^5-Cp)Pd(η^3-allyl)	0.2	L9	0.22	10	5	10	17.6
(η^5-Cp)Pd(η^3-allyl)	0.2	L10	0.22	10	5	10	2.6
(η^5-Cp)Pd(η^3-allyl)	0.2	L11	0.22	10	5	10	1.9
(η^5-Cp)Pd(η^3-allyl)	0.2	L12	0.22	10	5	10	0.8
(η^5-Cp)Pd(η^3-allyl)	0.2	L13	0.22	10	5	10	9.3
(η^5-Cp)Pd(η^3-allyl)	0.2	L14	0.22	10	5	10	0
(η^5-Cp)Pd(η^3-allyl)	0.2	L15	0.22	10	5	10	0.9
(η^5-Cp)Pd(η^3-allyl)	0.2	L16	0.22	10	5	10	0
(η^5-Cp)Pd(η^3-allyl)	0.2	L17	0.22	10	5	10	0
(η^5-Cp)Pd(η^3-allyl)	0.2	L18	0.22	10	5	10	0.5
(η^5-Cp)Pd(η^3-allyl)	0.2	L19	0.22	10	5	10	0
(η^5-Cp)Pd(η^3-allyl)	0.2	L20	0.22	10	5	10	0

[a] Average of 2 independent runs. [b] Average of 3 independent runs. [c] Zn (10 mmol) added to reduce [Pd].

General procedure for one-pot synthesis of sodium acrylate. A 60 mL steel autoclave was charged with (COD)$PdCl_2$ (0.10 or 0.20 mmol), 1,2-bis(dicyclohexylphosphino)ethane (0.11 or 0.22 mmol), base (20 mmol), Zn (10 mmol), and THF (30 mL) in an argon glovebox. The autoclave was removed from the glovebox and charged with ethylene (10 bar) while stirring for 15 min. followed by CO_2 (20 bar, *i.e.* in total 30 bar) while stirring for 15 min. at 20 °C. The autoclave was sealed and heated to the desired temperature (internal temperature of 100, 120 or 145 °C) for 20 h while stirring at 300 rpm with an overhead stirrer. The autoclave was cooled to 20 °C, the pressure was released, and the crude reaction mixture ws transferred to a 100 mL glass bottle with D_2O (15 mL) to wash the autoclave. Sodium 3-(trimethylsilyl)-2,2,3,3-d_4-propionate (21.6 mg, 130 μmol) was dissolved in D_2O (5 mL) and added to the glass bottle as an internal standard. Additionally, the vial was rinsed with D_2O (5 mL). Et_2O (40 mL) was added to the aqueous phase, shaken, and the layers were allowed to separate. An aliquot of the aqueous phase (2 mL) was removed with a syringe, centrifuged to separate residual Zn, and the liquid was transferred to a glass NMR tube for analysis. The TON was determined by ^{1}H NMR (200 MHz, 70 scans) according to the ratio of sodium acrylate to the standard sodium 3-(trimethylsilyl)-2,2,3,3-d_4-propionate.

General procedure for the synthesis of sodium salts of acrylate derivatives. In the glovebox, [Pd(COD)Cl_2] (0.10 mmol, 1 equiv), dcpe (0.11 mmol, 1.1 equiv), sodium 2-fluorophenolate (30.0 mmol, 300 equiv), Zn (10.0 mmol, 100 equiv) and butadiene (30.0 mmol, 300 equiv, 20 wt% in toluene) or 1,3-pentadiene (10.0 mmol, 100 eqiuv) were introduced in the autoclave together with THF (30 mL). The closed autoclave was pressurized outside the glovebox with CO_2 (20 bar, 15 min equilibration time) at 25 °C. The reaction mixture was stirred (300 rpm) at 145 °C for 20 h. After cooling to room temperature the pressure was released and the crude reaction mixture was transferred to a 100 mL glass bottle. The autoclave was washed with D_2O (15 mL). Sodium 3-(trimethylsilyl)-2,2,3,3-d_4-propionate (0.13 mmol) in D_2O (5 mL) was added to the reaction mixture as internal standard. The vial was washed with additional D_2O (5 mL). The reaction mixture was layered with Et_2O (40 mL) and the aqueous phase (2 mL) was centrifuged to facilitate phase

separation. The corresponding sodium salt was quantified by ^{1}H-NMR (200 MHz, 70 scans) and the turnover number (TON) was calculated accordingly.

Sodium (E)-penta-2,4-dienoate. ^{1}H NMR (200 MHz, D_2O): δ 5.44 (dd, *J* = 10.0, 0.7 Hz, 1H), 5.58 (dd, *J* = 17.0, 0.7 Hz, 1H), 5.97 (d, *J* = 15.4 Hz, 1H), 6.52 (dt, *J* = 17.0, 10.4 Hz, 1H), 7.00 (dd, *J* = 15.5, 10.8 Hz, 1H). ^{13}C{H} NMR (101 MHz, D_2O): δ 123.6 (CH_2), 127.9 (CH), 135.4 (CH), 141.5 (CH), 175.9 (CO).

Sodium sorbate. ^{1}H NMR (400 MHz, D_2O): δ 1.79 (d, *J* = 6.7 Hz, 3H), 5.80 (dd, *J* = 15.4, 0.6 Hz, 1H), 6.07 (dq, *J* =, 1H), 6.24 (dddd, *J* = 15.1, 10.5, 1.4, 0.5 Hz, 1H), 6.97 (dd, *J* = 15.4, 10.6 Hz, 1H). ^{13}C{H} NMR (101 MHz, D_2O): δ 17.8 (CH_3), 124.5 (CH), 129.7 (CH), 137.9 (CH), 142.0 (CH), 176.4 (CO).

III. X-ray Crystallographic Data

Preparation of Kolbe-Schmitt product (dcpe)Pd(OPhFCO$_2$) (**6**). A 60 mL steel autoclave was charged with sodium 2-fluorophenolate (2.956 g, 20.0 mmol), Zn powder (654 mg, 10.0 mmol), dcpe (93 mg, 22 μmol), (COD)$PdCl_2$ (57 mg, 20 μmol), and THF (30.0 mL). The autoclave was sealed, taken out of the glovebox, and charged with ethylene (10 bar) for 15 min while stirring at 300 rpm with an overhead stirrer. The autoclave was then charged with CO_2 (20 bar) for 15 min while stirring (total 30 bar). The autoclave was sealed and heated to 145 °C for 20 h. After cooling to *ca*. 30 °C the autoclave was depressurized, opened to air, and the content was transferred to a 100 mL bottle. The autoclave was washed with D_2O (25 mL). Et_2O (*ca*. 20 mL) was added to the bottle, and the bottle was shaken vigorously. The Et_2O layer was removed via pipette and the solvent was removed *in vacuo*. A small portion of the solid was taken into Et_2O, filtered through a pipette with celite and placed at –35 °C, yielding crystals of **6** suitable for X-ray characterization and elemental analysis. Elemental analysis calcd. for $C_{45}H_{61}F_3O_5P_2Pd$ (2 eq. phenol): C 59.57, H 6.78. Found: C 59.64, H 6.97. ^{31}P NMR (81 MHz, THF-d_8, 20 °C): δ 86.24. Additional NMR characterization not possible due to decomposition, and a lack of material (only minor side product).

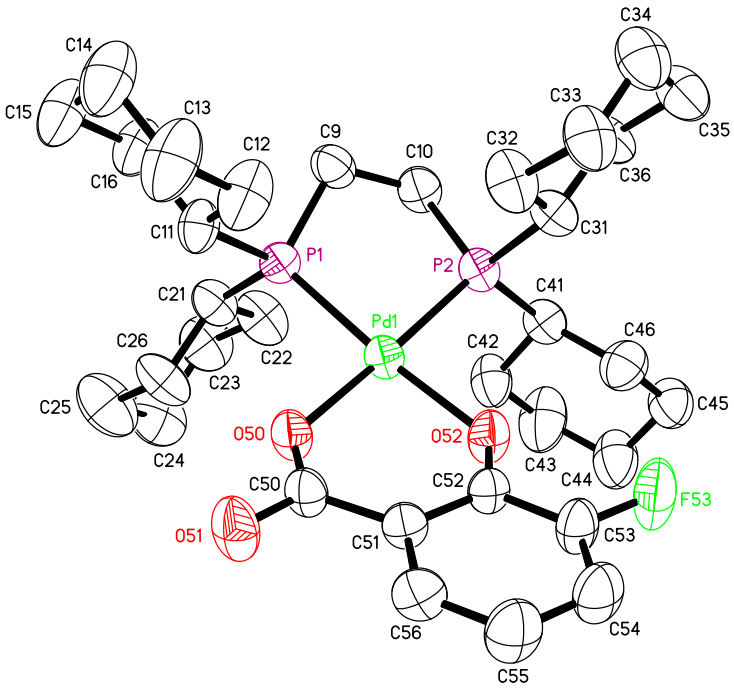

Table S2: Crystal data and structure refinement for **6**.

Empirical formula	$C_{39}H_{56}F_2O_4P_2Pd$
Formula weight	795.17
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1/n$
Z	8
Unit cell dimensions	a = 17.3557(15) Å α = 90°.
	b = 17.2752(14) Å β = 106.717(2)°.
	c = 27.490(2) Å γ = 90°.
Volume	7893.7(11) $Å^3$
Density (calculated)	1.34 g/cm^3
Absorption coefficient	0.60 mm^{-1}
Crystal shape	plate
Crystal size	0.260 x 0.180 x 0.040 mm^3
Crystal colour	colourless
Theta range for data collection	1.4 to 20.9°.
Index ranges	-17≤h≤17, -17≤k≤17, -27≤l≤25
Reflections collected	44695
Independent reflections	8348 (R(int) = 0.1229)
Observed reflections	5631 (I > 2σ(I))
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.97 and 0.82
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	8348 / 1460 / 973
Goodness-of-fit on F^2	1.08
Final R indices (I>2sigma(I))	R1 = 0.094, wR2 = 0.191
Largest diff. peak and hole	0.94 and -1.03 $eÅ^{-3}$

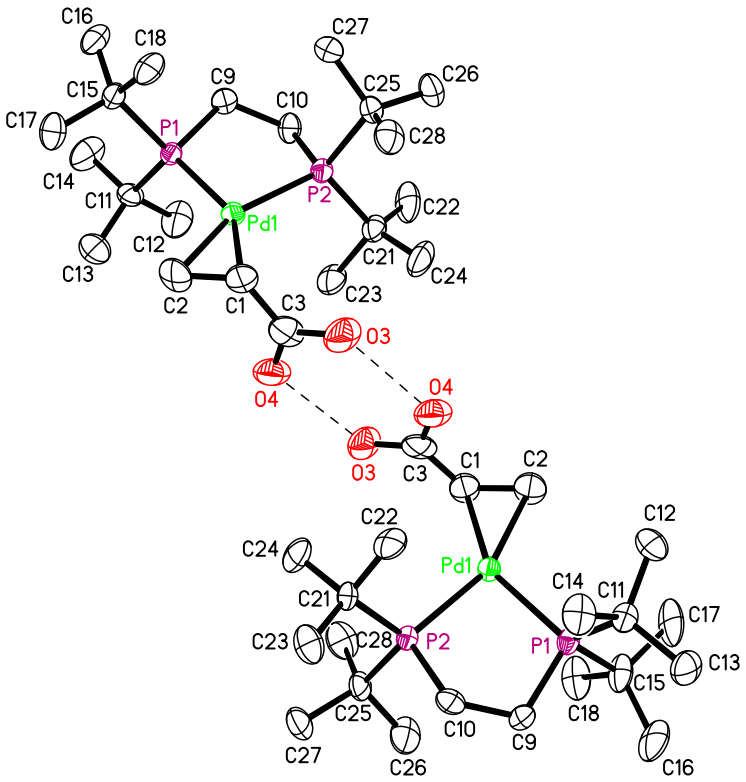

Table S3: Crystal data and structure refinement for **2**.

Empirical formula	$C_{21}H_{44}O_2P_2Pd$	
Formula weight	496.90	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	orthorombic	
Space group	$Pca2_1$	
Z	8	
Unit cell dimensions	a = 15.9351(15) Å	α = 90°.
	b = 14.7211(14) Å	β = 90°.
	c = 21.273(2) Å	γ = 90°.
Volume	4990.3(8) Å^3	
Density (calculated)	1.32 g/cm^3	
Absorption coefficient	0.88 mm^{-1}	
Crystal shape	polyhedron	
Crystal size	0.11 x 0.09 x 0.09 mm^3	
Crystal colour	colourless	
Theta range for data collection	1.9 to 28.7°.	
Index ranges	-11≤h≤11, -33≤k≤27, -20≤l≤21	
Reflections collected	57263	
Independent reflections	12866 (R(int) = 0.1025)	
Observed reflections	8944 (I >2σ(I))	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.92 and 0.91	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	12866 / 0 / 471	
Goodness-of-fit on F^2	1.02	
Final R indices (I>2□(I))	R1 = 0.050, wR2 = 0.079	
Largest diff. peak and hole	0.42 and -0.55 eÅ^{-3}	

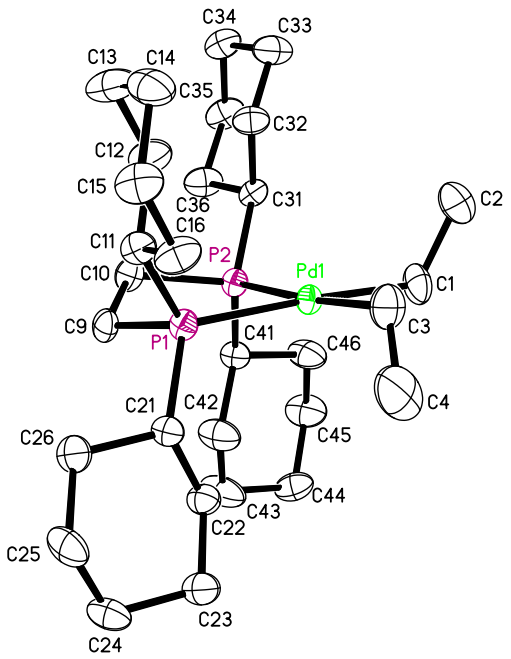

Table S4: Crystal data and structure refinement for **3**.

Empirical formula	$C_{30}H_{58}P_2Pd$
Formula weight	587.10
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	Cc
Z	4
Unit cell dimensions	a = 11.1923(13) Å α = 90°.
	b = 16.4379(19) Å β = 101.0818(18)°.
	c = 16.7601(19) Å γ = 90°.
Volume	3026.0(6) Å^3
Density (calculated)	1.29 g/cm^3
Absorption coefficient	0.74 mm^{-1}
Crystal shape	polyhedron
Crystal size	0.260 x 0.150 x 0.130 mm^3
Crystal colour	colourless
Theta range for data collection	2.2 to 28.7°.
Index ranges	-15≤h≤14, -22≤k≤22, -22≤l≤21
Reflections collected	11216
Independent reflections	6847 (R(int) = 0.0265)
Observed reflections	6422 (I > 2σ(I))
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.87 and 0.81
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6847 / 2 / 298
Goodness-of-fit on F^2	1.07
Final R indices (I>2sigma(I))	R1 = 0.033, wR2 = 0.057
Absolute structure parameter	0.002(15)
Largest diff. peak and hole	0.70 and -0.43 eÅ^{-3}

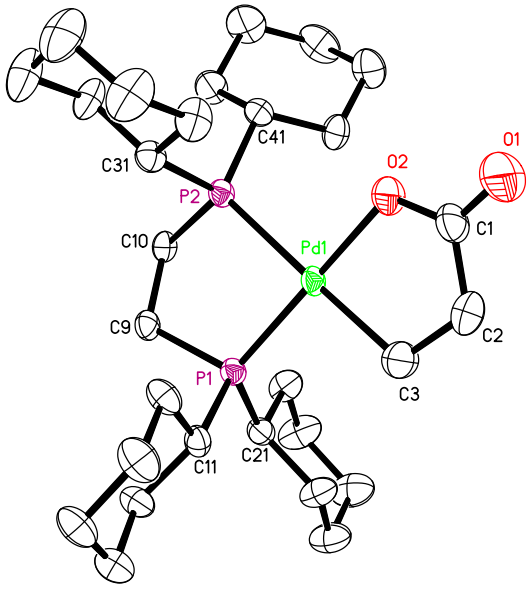

Table S5: Crystal data and structure refinement for **5**.

Empirical formula	$C_{31.50}H_{56}O_2P_2Pd$	
Formula weight	635.10	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	C2/c	
Z	8	
Unit cell dimensions	a = 28.266(2) Å	α = 90°.
	b = 13.8216(11) Å	β = 118.016(2)°.
	c = 18.2436(14) Å	γ = 90°.
Volume	6292.2(9) Å^3	
Density (calculated)	1.34 g/cm^3	
Absorption coefficient	0.72 mm^{-1}	
Crystal shape	polyhedron	
Crystal size	0.170 x 0.100 x 0.100 mm^3	
Crystal colour	colourless	
Theta range for data collection	1.9 to 24.9°.	
Index ranges	-33≤h≤33, -16≤k≤16, -21≤l≤21	
Reflections collected	24383	
Independent reflections	5417 (R(int) = 0.0800)	
Observed reflections	3960 (I > 2σ(I))	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.94 and 0.86	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	5417 / 50 / 352	
Goodness-of-fit on F^2	1.06	
Final R indices (I>2sigma(I))	R1 = 0.052, wR2 = 0.083	
Largest diff. peak and hole	0.49 and -0.82 eÅ^{-3}	

IV. Representative NMR Spectra

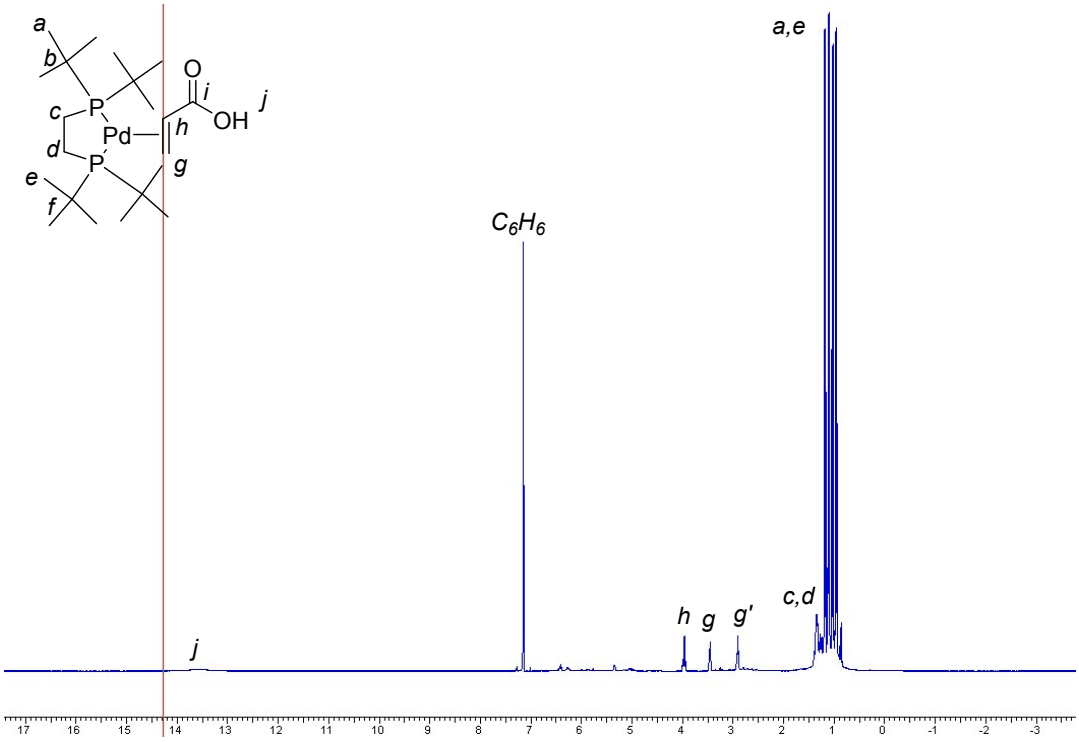

Figure S3. ^{1}H NMR spectrum (C_6D_6, 600 MHz) of (d^tbpe)Pd(η^2-CH_2CHCO_2H) (**2**).

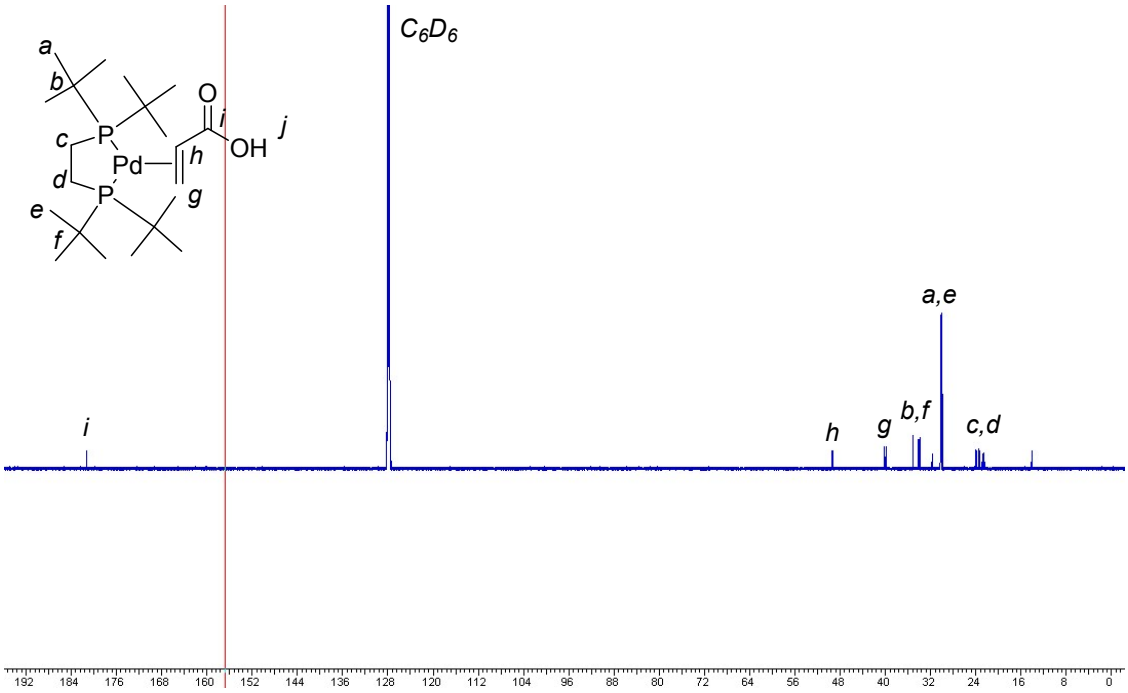

Figure S4. ^{13}C NMR spectrum (C_6D_6, 151 MHz) of (d^tbpe)Pd(η^2-CH_2CHCO_2H) (**2**).

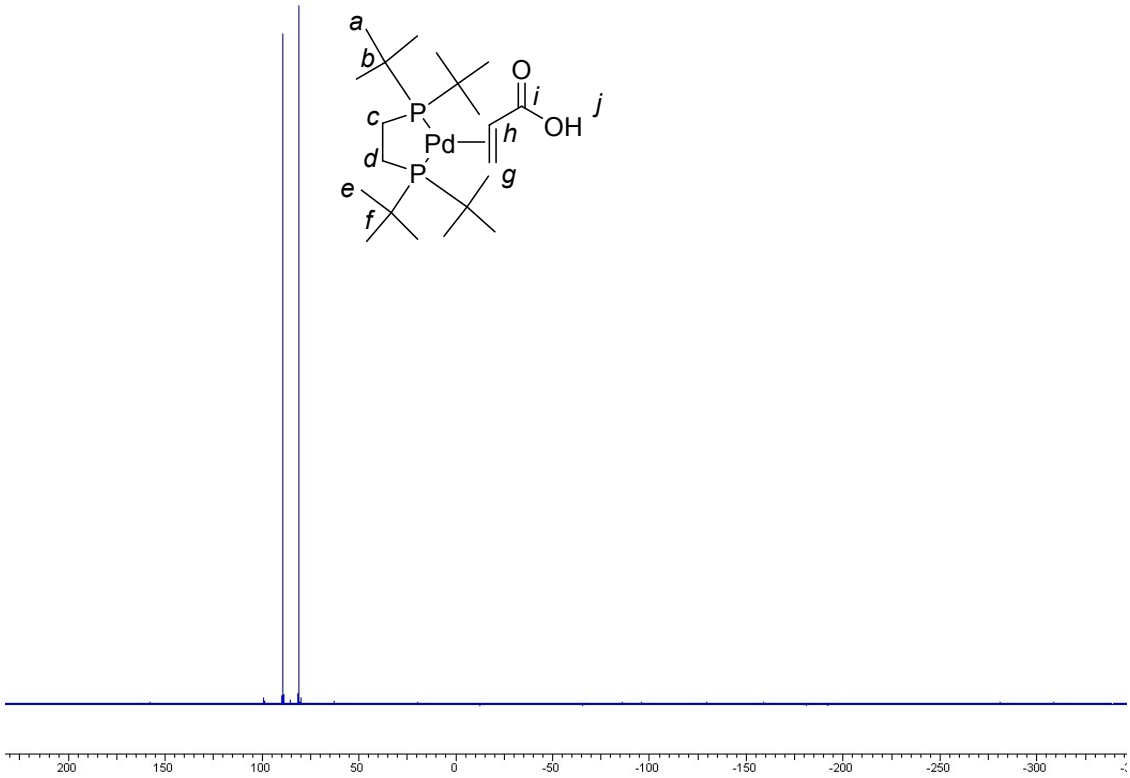

Figure S5. ^{31}P NMR spectrum (C_6D_6, 243 MHz) of of (d^{t}bpe)Pd(η^2-CH_2CHCO_2H) (**2**).

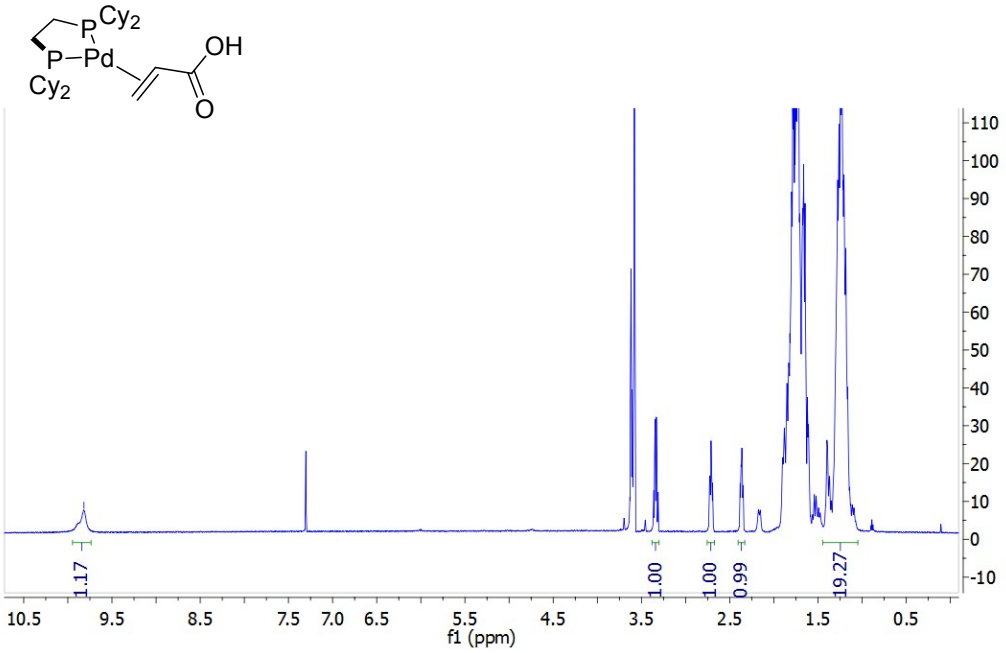

Figure S6. ^{1}H NMR spectrum (THF-d_8, 600 MHz) of (dcpe)Pd(η^2-CH_2CHCO_2H) (**4**).

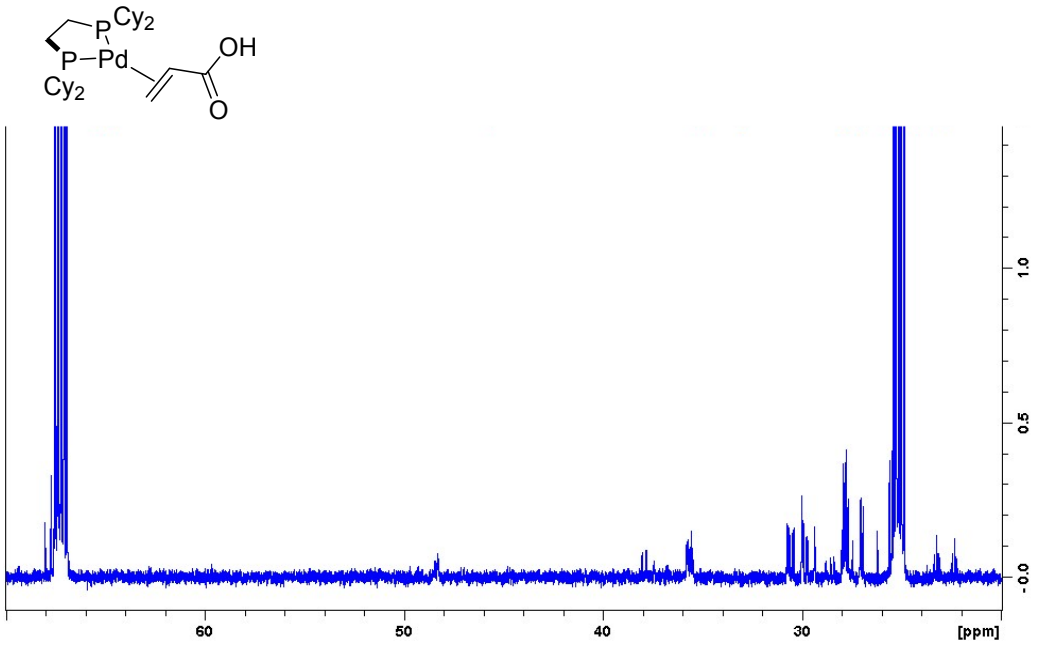

Figure S7. ^{13}C NMR spectrum (THF-d_8, 151 MHz) of (dcpe)Pd(η^2-CH_2CHCO_2H) (**4**).

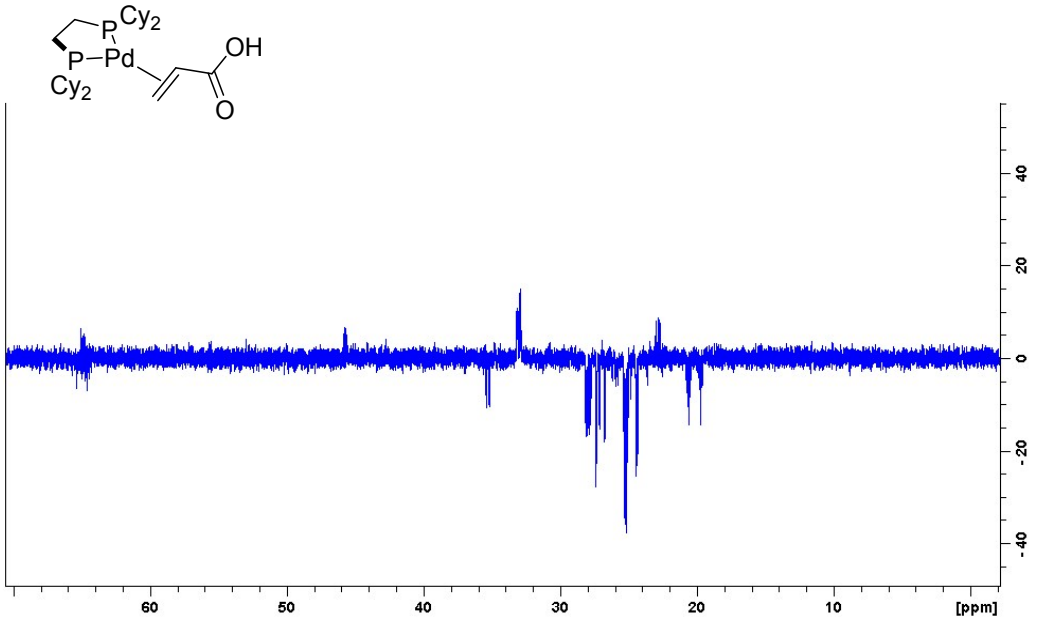

Figure S8. ^{13}C DEPT-135 NMR spectrum (THF-d_8, 151 MHz) of (dcpe)Pd(η^2-CH_2CHCO_2H) (**4**).

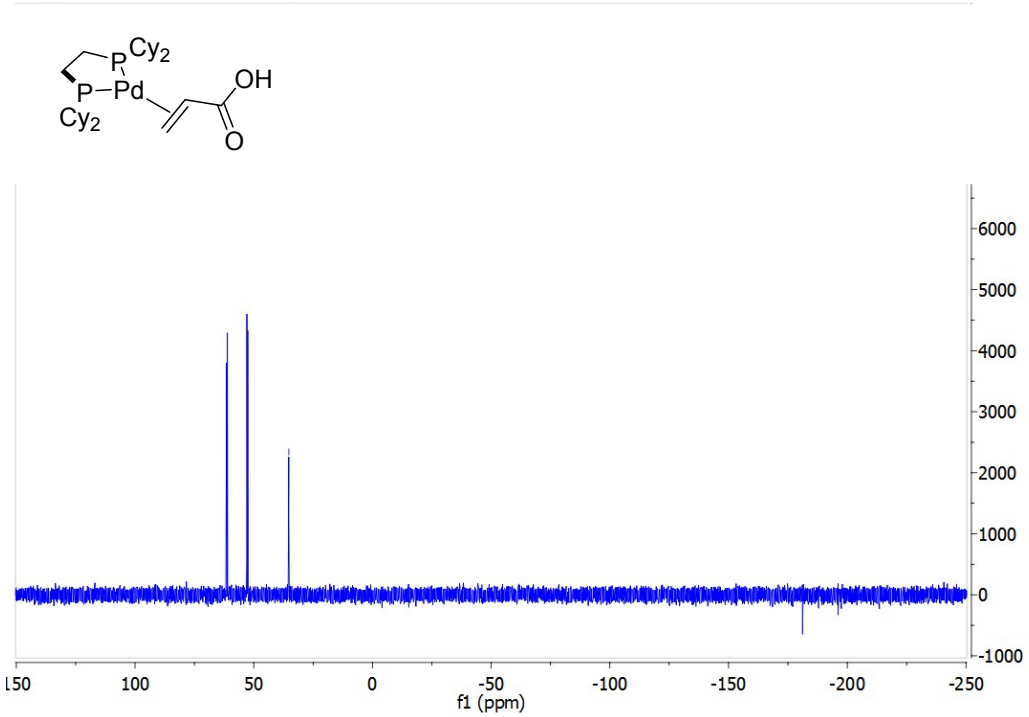

Figure S9. ^{31}P NMR spectrum (THF-d_8, 81 MHz) of (dcpe)Pd(η^2-CH_2CHCO_2H) (**4**). Small amount of bis-ligand compound present.

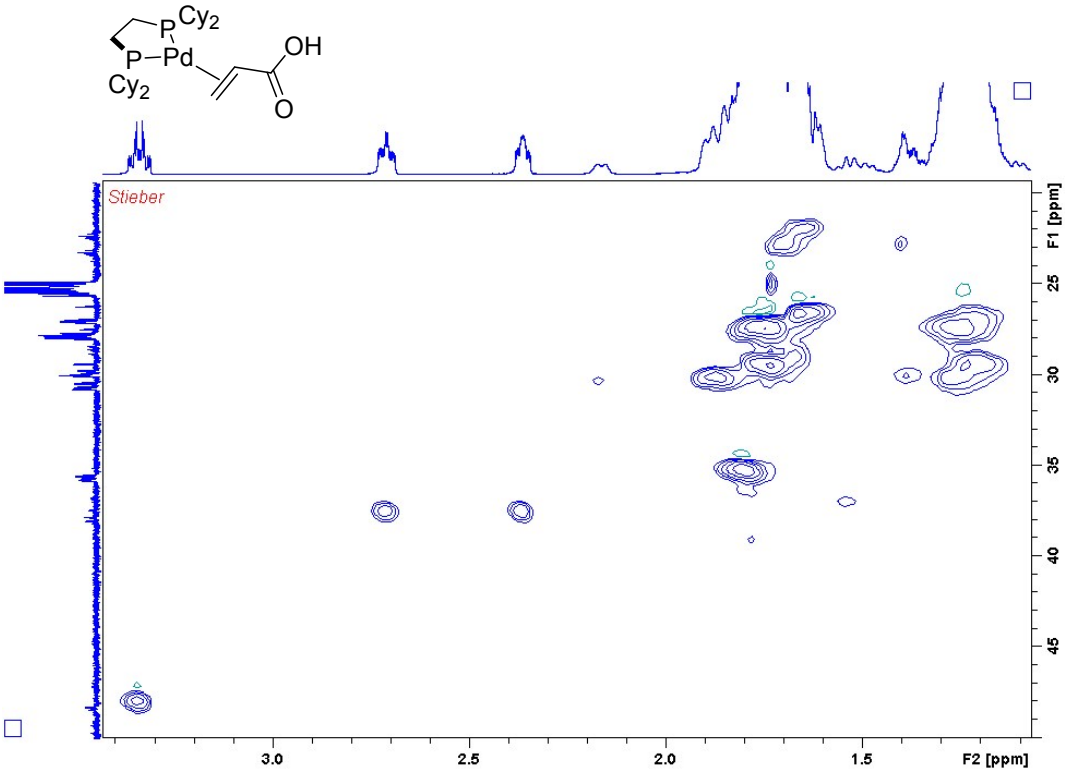

Figure S10. HSQC NMR spectrum (THF-d_8, 600 MHz) of (dcpe)Pd(η^2-CH_2CHCO_2H) (**4**).

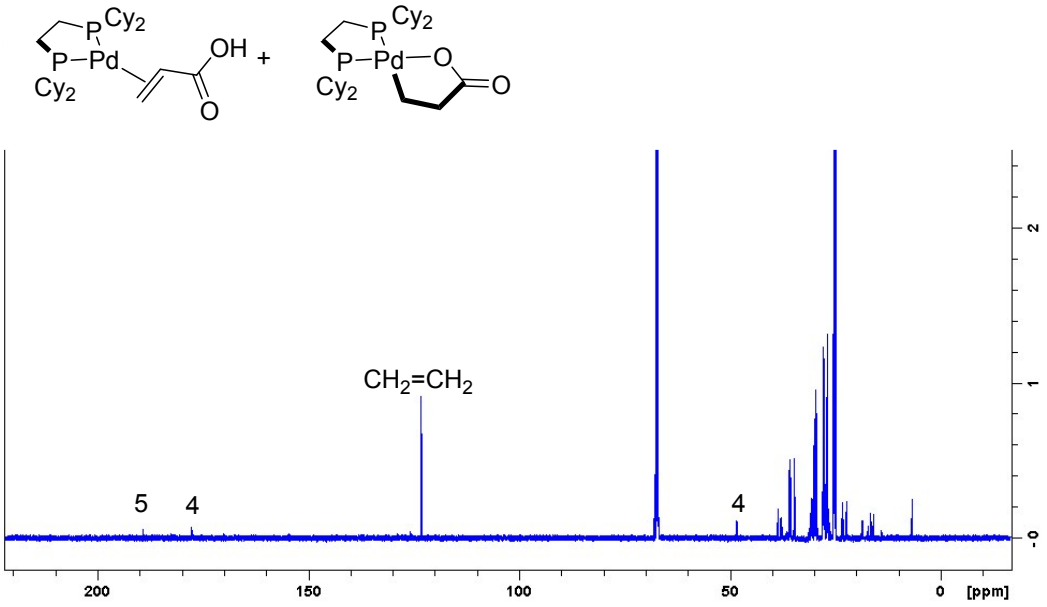

Figure S11. ^{13}C NMR spectrum (THF-d_8, 151 MHz) of a mixture of (dcpe)Pd(η^2-CH_2CHCO_2H) (**4**) and (dcpe)Pd(-CH_2CHCO_2-) (**5**).

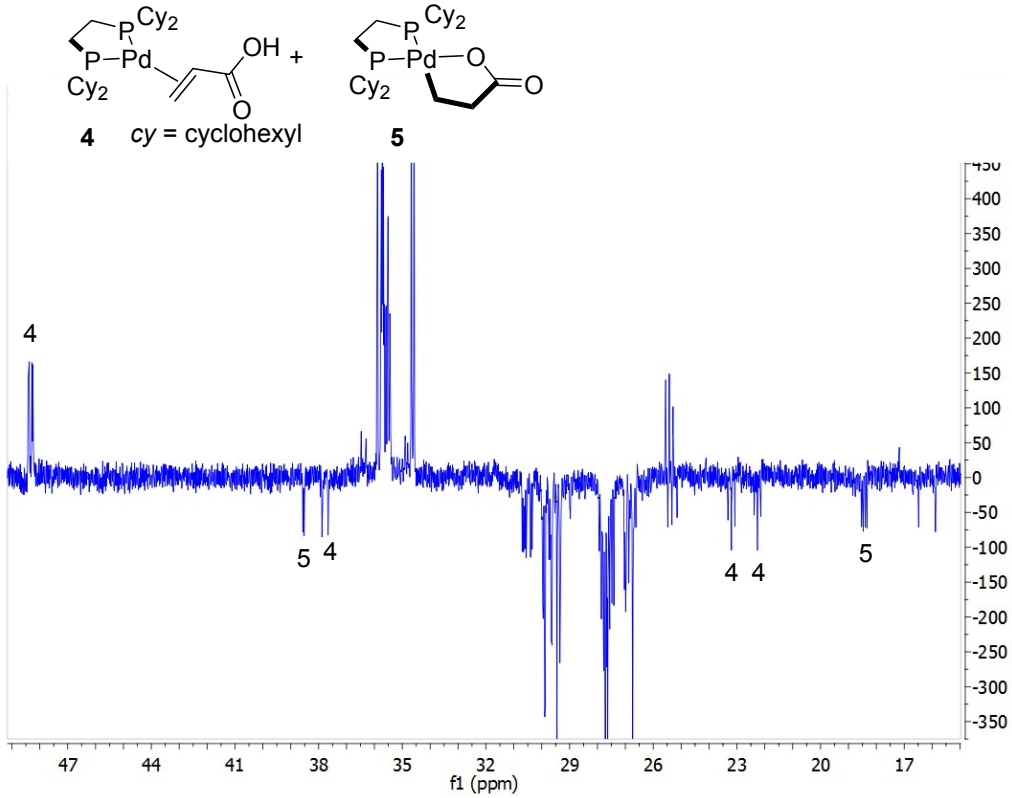

Figure S12. ^{13}C DEPT-135 NMR spectrum (THF-d_8, 151 MHz) of a mixture of **4** and **5**.

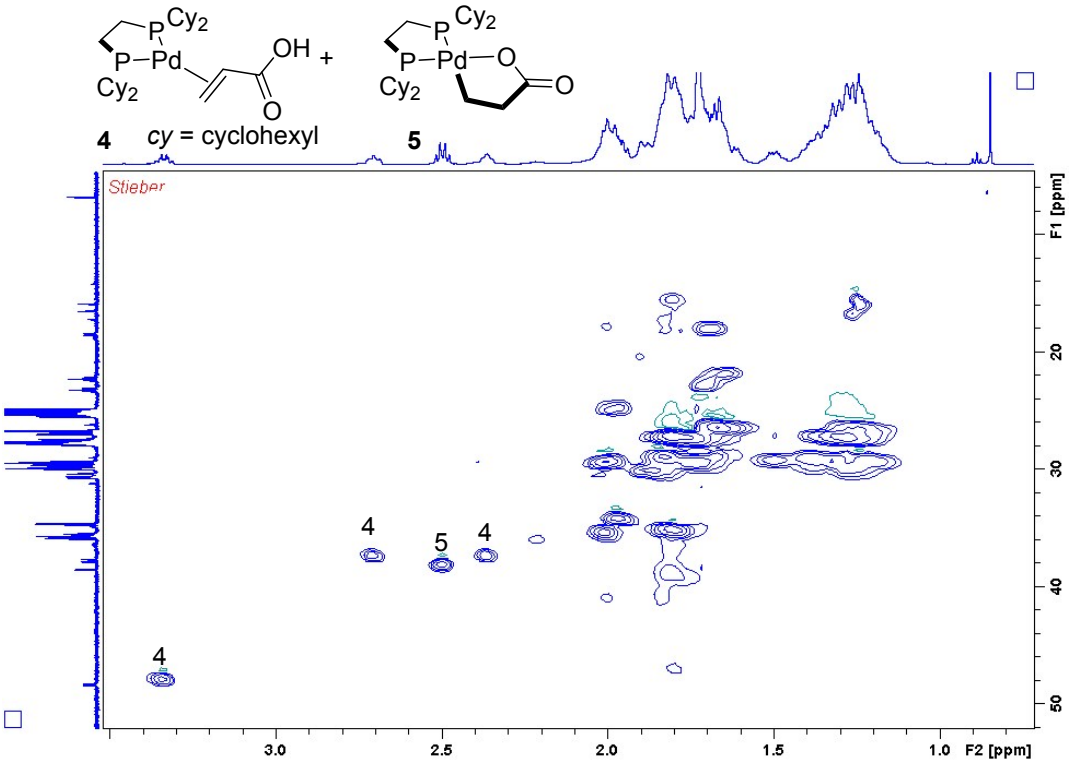

Figure S13. HSQC NMR spectrum (THF-d_8, 243 MHz) of a mixture of **4** and **5**.

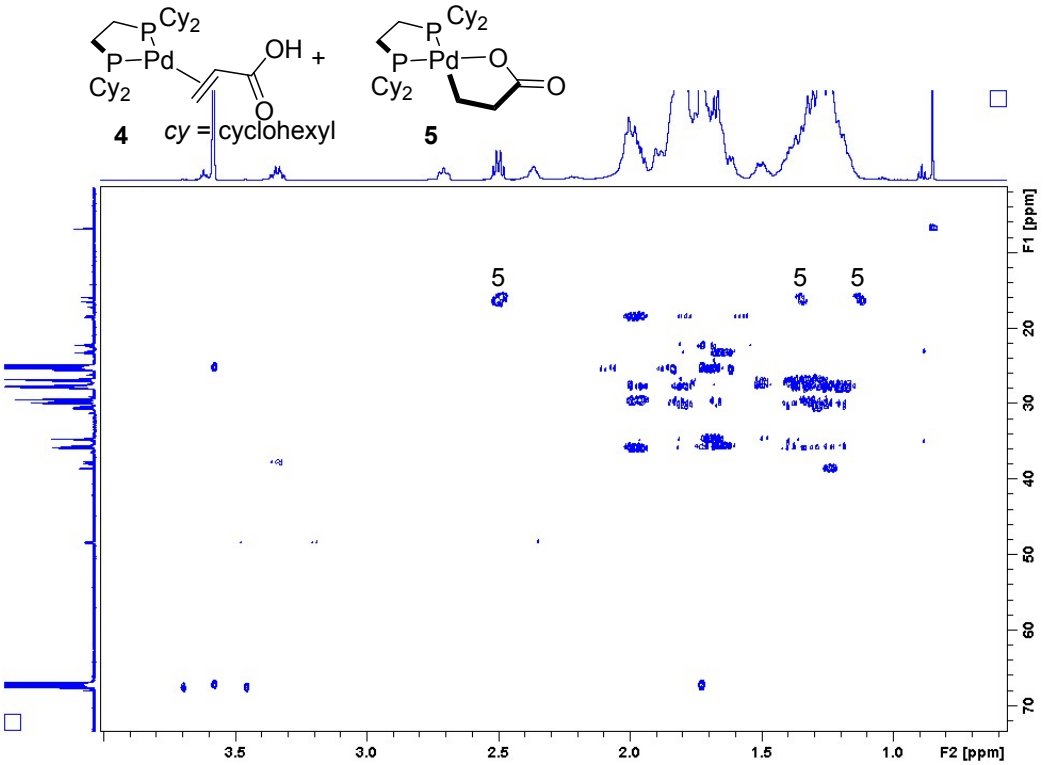

Figure S14. HMBC NMR spectrum (THF-d_8, 243 MHz) of a mixture of of **4** and **5**.

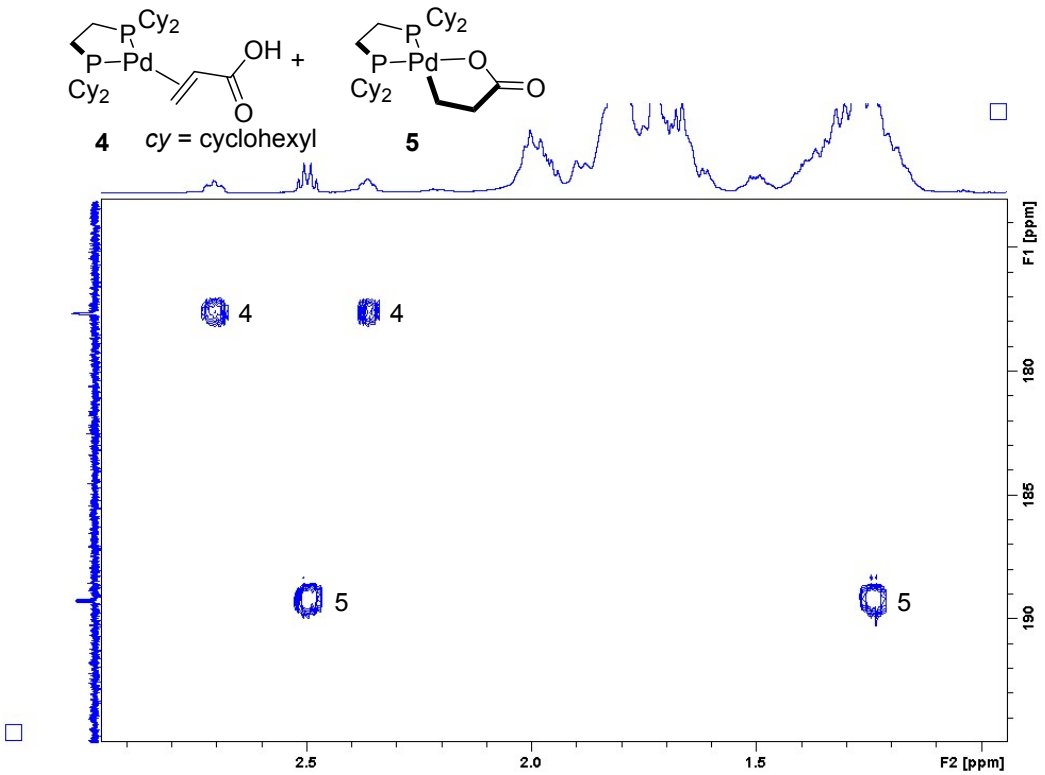

Figure S15. HMBC NMR spectrum (THF-d_8, 243 MHz, carbonyl region) of a mixture of of **4** and **5**.

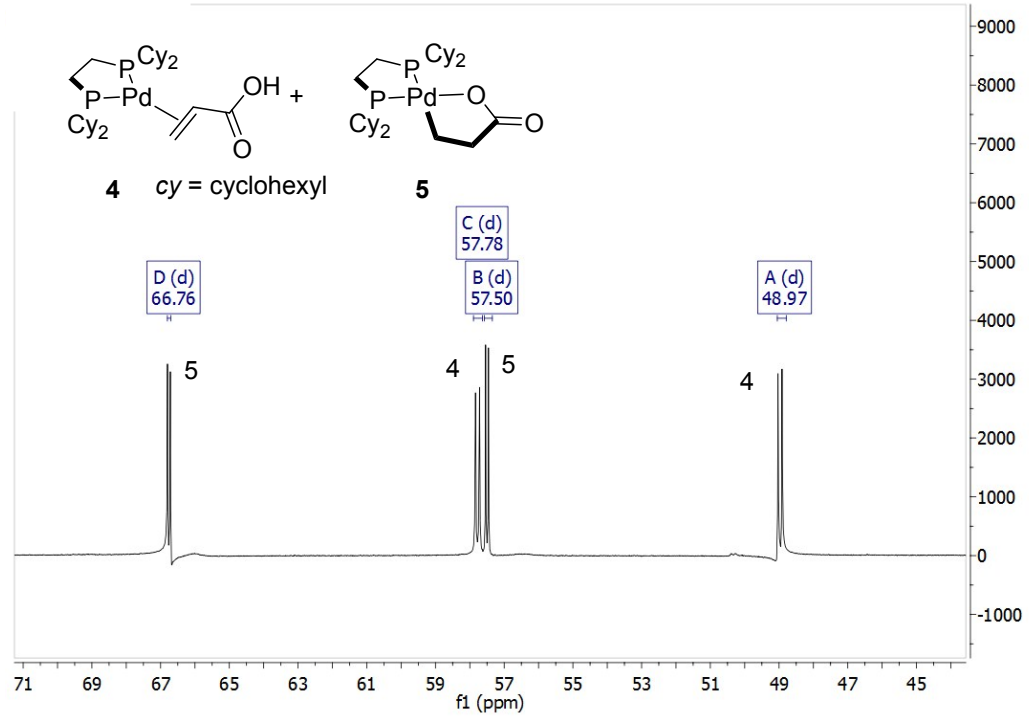

Figure S16. ^{31}P NMR spectrum (THF-d_8, 243 MHz) of a mixture of of **4** and **5**.

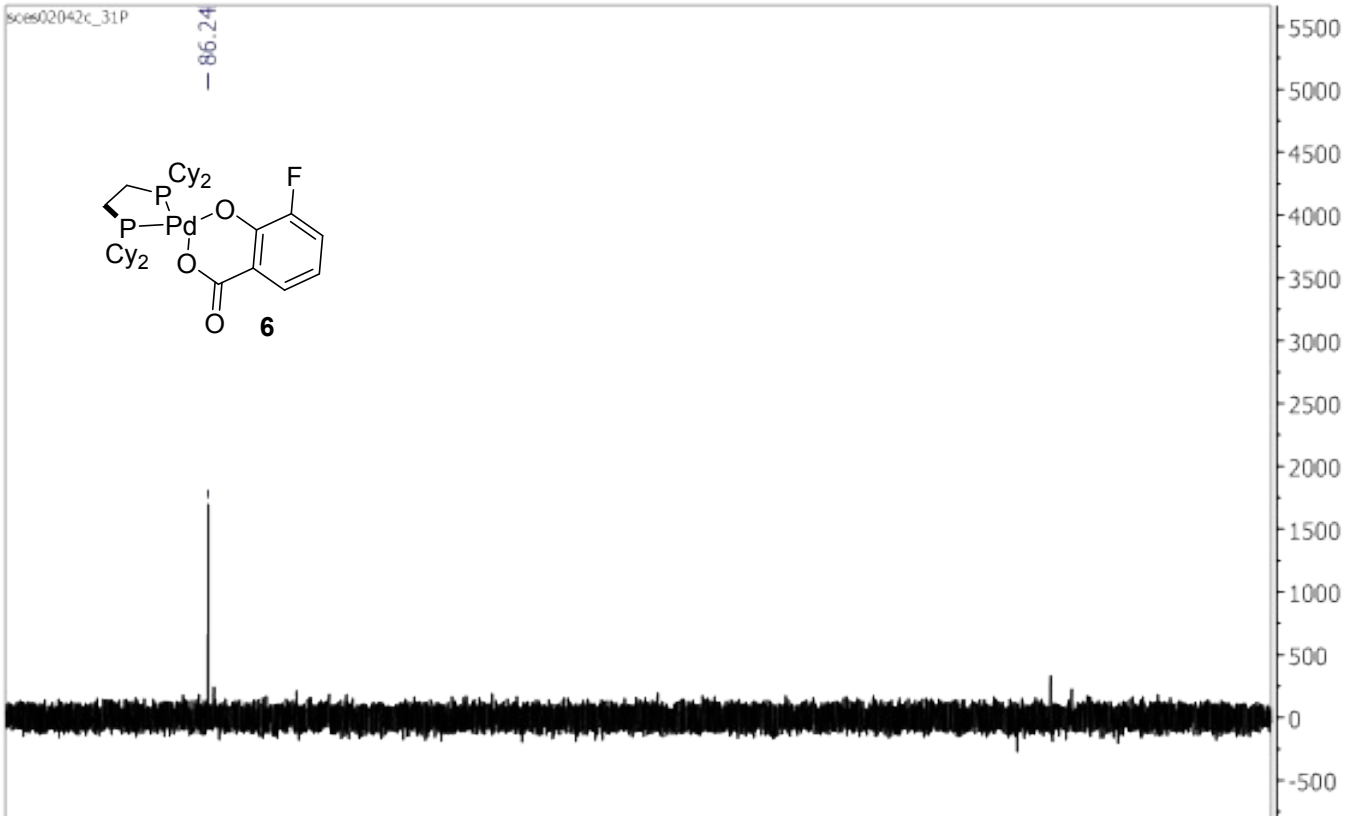

Figure S17. ^{31}P NMR spectrum (THF-d_8, 81 MHz) of (dcpe)Pd(OPhFCOO) (**6**).

IV. References

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