

SUPPORTING INFORMATION

Directing Selectivity to Aldehydes, Alcohols or Esters with Diphobane Ligands in Pd-Catalyzed Alkene Carbonylations

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General

Unless stated otherwise, all manipulations were performed under N₂ using standard Schlenk line techniques on a dual manifold vacuum/inert gas line or in an MBraun Labmaster DP glovebox. Glassware was dried at 150 °C overnight prior to use. Solvents and solutions were transferred using a positive pressure of nitrogen through stainless steel cannulas, or via plastic syringes for volumes less than or equal to 20 ml. Filtrations were performed using modified stainless-steel cannulas fitted with glass microfibre filters. Solvents used (pentane, toluene, THF, Et₂O and CH₂Cl₂) were dried using an Innovative Technology Pure Solv SPS-400. All solvents were stored in gas-tight graduated ampoules over 3 Å molecular sieves. CDCl₃ (99.8%) was freeze-pump-thaw degassed, dried, and stored over 3 Å molecular sieves in the glovebox. Syngas (CO:H₂ = 1:2) was obtained premixed from BOC and used as received without further purification.

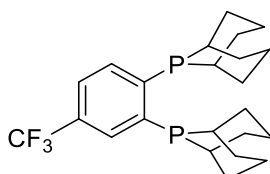
NMR spectra were recorded using Bruker AV400 spectrometers at 25 °C. ¹H and ¹³C chemical shifts, δ (in ppm), are given relative to Me₄Si and are referenced to the residual solvent peak. ¹³C chemical shifts were proton decoupled. ³¹P{¹H} chemical shifts were referenced externally in CDCl₃ to 85% H₃PO₄ (aq). Air or moisture sensitive samples were prepared inside the glovebox using oven-dried NMR tubes fitted with J. Young valves. NMR spectra are reported as follows: chemical shift (δ ppm), integration, multiplicity, coupling constant (Hz) and assignment. Multiplicities are given as follows (or combinations thereof): s – singlet, d – doublet, t – triplet, q – quartet, m – multiplet, br – broad. Detailed NMR assignments were elucidated via cross-referencing 2D NMR experiments (¹H,¹H-COSY and ¹H,¹³C-HSQC) with 1D NMR experiments (¹H, ¹³C{¹H}, ³¹P{¹H} and DEPT-135). Acquired data was processed and analysed by MestReNova version 11.0.0-17609.

Gas Chromatography (GC) was carried out on a Agilent 6890N Gas Chromatograph instrument fitted with a Agilent 7683 Automatic Liquid Sampler and FID detection on a HP-5 (5%-Phenyl)-methylpolysiloxane column, length 30 m, internal diameter 0.32 mm, film 0.25 μm, using helium as a carrier gas starting with a flow rate of 2 mL min⁻¹ for 1 min after injection then ramped at 1 mL min⁻² to 5 mL min⁻¹ and held for 5 min before ramping at 10 mL min⁻² to 25 mL min⁻¹ for the remainder of the run. The oven was kept isothermal at 40 °C for 5 min after injection then heated at 20 K min⁻¹ to 240 °C and kept isothermal for a further 5 min. Tandem Gas Chromatography/Mass Spectrometry (GC/MS) was carried out on a Agilent 7890B Gas Chromatograph instrument coupled with Agilent 5977B Mass Selective Detector.

High resolution mass spectrometry samples (HRMS; EI & ESI) were recorded by Angeline Seo using Agilent 6545B Q-TOF LC/MS. C, H and N elemental analysis was conducted by Angeline Seo using Thermo Scientific Flash 2000. CO and H₂ gases were purchased from Linde and used as received. 1,2-dibromo-4-(trifluoromethyl)benzene, 3,4-dibromoanisole, 1,2-dibromoveratrole and 1,2-dibromo-4-(*tert*-butyl)benzene were purchased from Fluorochem and used as received. Whatman® GF/C glass microfiber filters, 1-hexene, 1-octene, trans-4-octene, pent-4-enoic acid, pent-2-enoic acid (>95% *trans*), methanesulfonic acid, trifluoroacetic acid, sodium chloride, diglyme, 2-ethylhexanol, tetrakis(triphenylphosphine)palladium(0), 1,4-diazabicyclo[2.2.2]octane, xylene, 1,2-dibromobenzene and palladium(II) acetate were purchased from Sigma-Aldrich (now Merck) and used as received except for (a) alkenes which were treated over a bed of basic alumina to remove peroxides then degassed via sparging with nitrogen and stored over 3 Å molecular sieves under nitrogen, and (b) diglyme and 2-ethylhexanol solvents which were degassed via sparging with nitrogen and stored over 3 Å molecular sieves under nitrogen. 9-phosphabicyclononane (phobane, mixture of [3.3.1]*symmetric* and [4.2.1]*asymmetric* isomers) was separated as reported in literature¹ and the [3.3.1]*symmetric*-isomer used for ligand synthesis. Methyl 4-pentenoate and methyl 2-pentenoate were synthesized from pent-4-enoic acid and pent-2-enoic acid respectively via acid-catalyzed esterification by refluxing in MeOH with a catalytic amount of concentrate H₂SO₄.

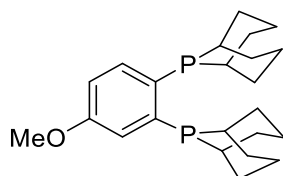
Ligand Synthesis

1,2-di(9-phosphabicyclo[3.3.1]nonan-9-yl)benzene (**L2**) and 1,2-di(9-phosphabicyclo[3.3.1]nonan-9-yl)ethane (**BCOPE**) were synthesized via reported procedures.²⁻³

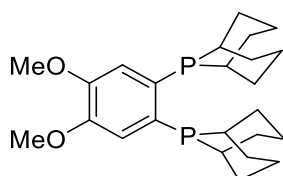


9,9'-(4-(trifluoromethyl)-1,2-phenylene)bis(9-phosphabicyclo[3.3.1]nonane) (L1) 9-phosphabicyclo[3.3.1]nonane (0.60 g, 4.20 mmol, 2.1 equiv), tetrakis(triphenylphosphine)palladium(0) (0.23 g, 0.20 mmol, 0.1 equiv), 1,4-diazabicyclo[2.2.2]octane (1.12 g, 10.0 mmol, 5.0 equiv) and 1,2-dibromo-4-(trifluoromethyl)benzene (0.61 g, 2.00 mmol, 1.0 equiv) were taken up in xylenes (15 mL) then stirred at 140 °C for 72 h. The resulting mixture was filtered

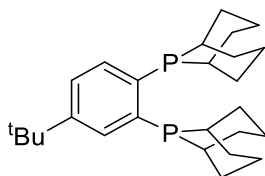
via cannula fitted with glass microfiber filter and the filtrate concentrated under vacuum to give a red solid. The red solid was flashed through a short pad of silica with toluene then washed with pentane (2 x 10 mL), MeOH (2 x 10 mL) and dried under vacuum to yield 9,9'-(4-(1,1,1-trifluoromethyl)-1,2-phenylene)bis(9-phosphabicyclo[3.3.1]nonane) as an off-white powder (0.40 g, 47%). ¹H (400 MHz, CDCl₃): δ 7.53 – 7.48 (1H, m, ArH), 7.43 – 7.37 (2H, m, ArH), 2.71 (4H, br.s, CH), 2.29 – 2.07 (10H, m, CH₂), 2.00 – 1.84 (6H, m, CH₂), 1.80 – 1.69 (6H, m, CH₂) and 1.37 – 1.28 (2H, m, CH₂). ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 147.5 (dd, ¹J_{CP}=34Hz, ²J_{CP}=14Hz), 143.7 (dd, ¹J_{CP}=34Hz, ²J_{CP}=14Hz), 131.3 (dd, ²J_{CP}=9Hz, ³J_{CP}=3Hz), 127.9 (q, CCF₃, ²J_{CF}=33Hz), 127.7 (dd, ²J_{CP}=9Hz, ³J_{CP}=3Hz), 124.5 (q, CF₃, ¹J_{CF} = 270 Hz), 122.3 (br.s), 32.1 (dd, J = 15 Hz, 4 Hz), 25.6 (dd, J = 15 Hz, 4 Hz), 24.8 (quint, J = 7 Hz), 22.9 (br.s) and 21.9 (s) ppm. ³¹P{¹H} NMR (162 MHz, CDCl₃): δ -15.7 and -16.2 ppm. ¹⁹F NMR (376 MHz, CDCl₃): δ -62.8 ppm. HR-MS (+ve ESI): m/z calculated for C₂₃H₃₂F₃P₂⁺, [M+H]⁺ 427.1926 required; 427.1942 found. Satisfactory elemental analysis could not be obtained due to the highly air-sensitive nature of the compound.



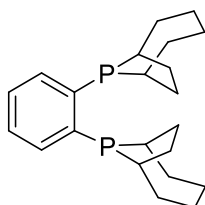
9,9'-(4-methoxy-1,2-phenylene)bis(9-phosphabicyclo[3.3.1]nonane) (L3) 9-phosphabicyclo[3.3.1]nonane (0.65 g, 4.52 mmol, 2.2 equiv), tetrakis(triphenylphosphine)palladium(0) (0.29 g, 0.21 mmol, 0.1 equiv), 1,4-diazabicyclo[2.2.2]octane (0.69 g, 6.15 mmol, 3.0 equiv) and 1,2-dibromoanisole (0.3 mL, 2.00 mmol, 1.0 equiv) were taken up in xylenes (15 mL) then stirred at 140 °C for 16 h. The resulting mixture was filtered via cannula fitted with glass microfiber filter and the filtrate concentrated under reduced pressure at 65 °C to give a reddish-brown solid. The residue was washed with pentane (2 x 10 mL) then flashed through a short pad of silica with toluene and subsequently washed with MeOH (2 x 20 mL) to yield 9,9'-(4-methoxy-1,2-phenylene)bis(9-phosphabicyclo[3.3.1]nonane) as a white solid (0.44 g, 54%). ¹H (400 MHz, CDCl₃): δ 7.23 – 7.18 (1H, m, ArH), 6.89 – 6.85 (1H, m, ArH), 6.76 (1H, dd, ³J_{HH} = 8.6 Hz, ⁴J_{HH} = 2.8 Hz, ArH), 3.80 (3H, s, CH₃), 2.67 (2H, br.s, PCH), 2.61 (2H, br.s, PCH), 2.26 – 1.92 (16H, m, CH₂), 1.77 – 1.66 (6H, m, CH₂) and 1.38 – 1.29 (2H, m, CH₂) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 157.8 (d, J = 2 Hz), 144.0 (dd, J = 31 Hz, 15 Hz), 132.8 (dd, J = 28 Hz, 14 Hz), 132.5 (dd, J = 9 Hz, 4 Hz), 117.4 (dd, J = 9 Hz, 4 Hz), 111.4 (s), 55.1 (s), 32.1 (dd, J = 15 Hz, 7 Hz), 25.6 (dd, J = 18 Hz, 4 Hz), 24.9 (m), 23.0 (dd, J = 10 Hz, 5 Hz) and 22.0 (d, J = 11 Hz) ppm. ³¹P{¹H} NMR (162 MHz, CDCl₃): δ -16.7 and -18.7 ppm. HR-MS (+ve ESI): m/z calculated for C₂₃H₃₅OP₂⁺, [M+H]⁺ 389.2158 required; 389.2165 found. Satisfactory elemental analysis could not be obtained due to the highly air-sensitive nature of the compound.



9,9'-(4,5-dimethoxy-1,2-phenylene)bis(9-phosphabicyclo[3.3.1]nonane) (L4) 9-phosphabicyclo[3.3.1]nonane (0.63 g, 4.40 mmol, 2.2 equiv), tetrakis(triphenylphosphine)palladium(0) (0.23 g, 0.20 mmol, 0.1 equiv), 1,4-diazabicyclo[2.2.2]octane (1.12 g, 10.0 mmol, 5.0 equiv) and 1,2-dibromoveratrole (0.59 g, 2.00 mmol, 1.0 equiv) were taken up in xylenes (15 mL) then stirred at 140 °C for 72 h. The resulting mixture was filtered via cannula fitted with glass microfiber filter and the filtrate concentrated under vacuum at 50 °C to give a dark red solid. The solid was washed with pentane (2 x 10 mL) then MeOH (2 x 10 mL) and dried under vacuum to yield 9,9'-(4,5-dimethoxy-1,2-phenylene)bis(9-phosphabicyclo[3.3.1]nonane) as a pale orange powder (0.28 g, 33%). ¹H (400 MHz, CDCl₃): δ 6.84 – 6.82 (2H, dd, J = 5.2 Hz, 2.3 Hz), 3.86 (6H, s, OCH₃), 2.62 (4H, br.s, PCH), 2.25 – 1.95 (16H, m, CH₂), 1.78 – 1.67 (6H, m, CH₂) and 1.37 – 1.28 (2H, m, CH₂) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 147.3 (s), 133.7 (dd, J = 29 Hz, 15 Hz), 129.0, 128.8, 128.6, 128.6, 114.4 (dd, J = 9 Hz, 5 Hz), 55.8 (s), 47.5 (s), 32.0 (d, J = 15 Hz), 25.6 (d, J = 4 Hz), 25.2 (dd, J = 13 Hz, 7 Hz), 23.0 (d, J = 5 Hz) and 22.0 (s) ppm. ³¹P{¹H} NMR (162 MHz, CDCl₃): δ -17.7 ppm. HR-MS (+ve ESI): m/z calculated for C₂₄H₃₇O₂P₂⁺, [M+H]⁺ 419.2263 required; 419.2276 found. Elem. Anal. Calcd for C₂₄H₃₆O₂P₂: C, 68.88; H, 8.67. Found: C, 68.72; H, 8.54.



9,9'-(4-(tert-butyl)-1,2-phenylene)bis(9-phosphabicyclo[3.3.1]nonane) (L5) 9-phosphabicyclo[3.3.1]nonane (0.64 g, 4.48 mmol, 2.8 equiv), tetrakis(triphenylphosphine)palladium(0) (0.19 g, 0.16 mmol, 0.1 equiv), 1,4-diazabicyclo[2.2.2]octane (0.90 g, 8.00 mmol, 5.0 equiv) and 1,2-dibromo-4-(1,1-dimethylethyl)benzene (0.3 mL, 1.60 mmol, 1.0 equiv) were taken up in xylenes (15 mL) then stirred at 140 °C for 72 h. The resulting mixture was filtered via cannula fitted with glass microfiber filter and the filtrate concentrated under vacuum to give an orange solid. The solid was washed with MeOH (3 x 10 mL) then pentane (3 x 5 mL) to yield 9,9'-(4-(1,1-dimethylethyl)-1,2-phenylene)bis(9-phosphabicyclo[3.3.1]nonane) as an off-white powder (0.21 g, 32%). ¹H (400 MHz, CDCl₃): δ 7.33 – 7.29 (1H, m, ArH), 7.24 – 7.17 (2H, m, ArH), 2.68 (2H, br.s, PCH), 2.64 (2H, br.s, PCH), 2.31 – 1.89 (16H, m, CH₂), 1.77 – 1.67 (6H, m, CH₂) and 1.31 (11H, m, tBu & CH₂) ppm. ¹³C {¹H} NMR (101 MHz, CDCl₃): δ 148.2 (s), 141.3 (dd, J = 29 Hz, 14 Hz), 138.3 (dd, J = 29 Hz, 14 Hz), 130.9 (dd, J = 8 Hz, 4 Hz), 128.5 (dd, J = 8 Hz, 4 Hz), 123.0 (s), 34.6 (s), 32.1 (dd, J = 14 Hz, 5 Hz), 31.1 (s), 25.7 (t, J = 4 Hz), 24.9 (m), 23.1 (t, J = 5 Hz) and 22.1 (d, J = 8 Hz) ppm. ³¹P {¹H} NMR (162 MHz, CDCl₃): δ -16.7 and -18.3 ppm. HR-MS (+ve ESI): m/z calculated for C₂₆H₄₁P₂⁺, [M+H]⁺ 415.2678 required; 415.2692 found. Elem. Anal. Calcd for C₂₆H₄₀P₂: C, 75.33; H, 9.73. Found: C, 75.23; H, 9.45.

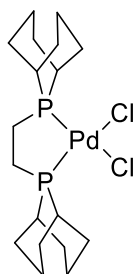


1,2-Di(9-phosphabicyclo[4.2.1]nonan-9-yl)benzene (L6) 9-phosphabicyclo[4.2.1]nonane (0.70 g, 4.92 mmol, 2.2 equiv), tetrakis(triphenylphosphine)palladium(0) (0.13 g, 0.11 mmol, 0.05 equiv), 1,4-diazabicyclo[2.2.2]octane (1.26 g, 11.2 mmol, 5.0 equiv) and 1,2-dibromobenzene (0.27 mL, 2.24 mmol, 1.0 equiv) were taken up in xylenes (15 mL) then stirred at 140 °C for 72 h. The resulting mixture was filtered and the filtrate concentrated under vacuum. The residue obtained was filtered through a short pad of silica with toluene (20 mL) then concentrated under reduced pressure to give a crude solid product. The crude product was triturated with MeOH (3 x 10 mL) and dried under vacuum to yield 9,9'-(1,2-phenylene)bis(9-phosphabicyclo[4.2.1]nonane) as a white solid (0.29 g, 37%). ¹H NMR (400 MHz, CDCl₃): δ 7.28 – 7.22 (2H, m, ArH), 7.17 – 7.11 (2H, m, ArH), 3.00 – 2.91 (4H, m, CH), 2.26 – 2.16 (4H, m, CH₂), 2.04 – 1.93 (4H, m, CH₂) and 1.86 – 1.50 ppm (16H, m, CH₂). ¹³C NMR (101 MHz, CDCl₃): δ 130.0, 127.0, 40.0, 40.0, 40.0, 35.0, 34.9, 34.8, 25.7, 25.7 and 25.6 ppm. ³¹P {¹H} NMR (162 MHz, CDCl₃): δ 3.8 ppm. HR-MS (+ve ESI): m/z calculated for C₂₂H₃₃P₂⁺, [M+H]⁺ 359.2052 required; 359.2066 found. Satisfactory elemental analysis could not be obtained due to the highly air-sensitive nature of the compound.

Pd Complex Synthesis

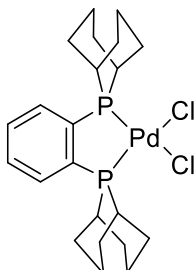
General procedure for synthesis of Pd(diphosphine)Cl₂ complexes

Diphosphine (0.1 mmol, 1 eq) and Pd(COD)Cl₂ (28.6 mg, 0.1 mmol, 1 eq) were dissolved in CH₂Cl₂ (2 mL) then stirred overnight. Volatiles were removed under vacuum to obtain the desired complex. Crystals suitable for single crystal x-ray diffraction were grown from slow vapor diffusion of cyclohexane into CH₂Cl₂ solutions of the complex. COD = 1,5-cyclooctadiene.

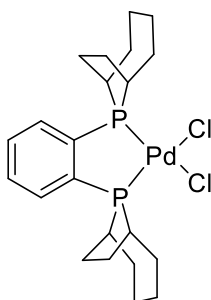


(1,2-di(9-phosphabicyclo[3.3.1]nonan-9-yl)ethane)dichloropalladium(II) complex, [Pd(BCOPE)Cl₂]
Synthesized via the general procedure for synthesis of Pd(diphosphine)Cl₂ complexes. Diphosphine = 1,2-di(9-

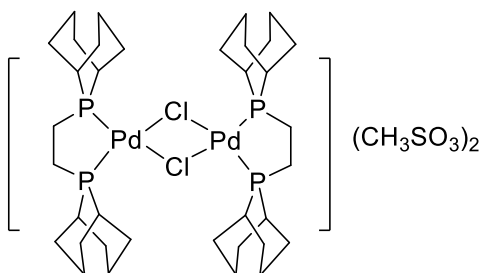
phosphabicyclo[3.3.1]nonan-9-yl)ethane (**BCOPE**). ^1H NMR (400 MHz, CD_2Cl_2): δ 3.38 (4H, br.s, *PCH*), 2.35 – 2.26 (4H, m, *CH*₂), 2.25 – 2.13 (6H, m, *CH*₂) and 2.10 – 1.69 (18H, m, *CH*₂) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_2Cl_2): δ 29.3, 29.2, 28.4, 28.2, 27.9, 27.7, 21.0 and 20.8 ppm. *Note: $^{13}\text{C}\{^1\text{H}\}$ NMR spectra signals (Figure S14) were weak, hence, ^1H - ^{13}C HSQC spectrum (Figure S16) is provided as additional experimental data in corroboration. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2): δ 51.3 ppm. HR-MS (+ve ESI): *m/z* calculated for $\text{C}_{18}\text{H}_{32}\text{Cl}_2\text{NaP}_2\text{Pd}^+$, $[\text{M}+\text{Na}]^+$ 509.0283 required; 509.0269 found. Elem. Anal. Calcd for $\text{C}_{18}\text{H}_{32}\text{Cl}_2\text{P}_2\text{Pd}\cdot 0.5\text{H}_2\text{O}$: C, 43.52; H, 6.70. Found: C, 43.68; H, 6.41.



(1,2-di(9-phosphabicyclo[3.3.1]nonan-9-yl)benzene)dichloropalladium(II) complex, $[\text{Pd}(\text{L2})\text{Cl}_2]$ Synthesized via the general procedure for synthesis of $\text{Pd}(\text{diphosphine})\text{Cl}_2$ complexes. Diphosphine = 1,2-di(9-phosphabicyclo[3.3.1]nonan-9-yl)benzene (**L2**). ^1H NMR (400 MHz, CD_2Cl_2): δ 8.11 – 8.04 (2H, m, *ArH*), 7.58 – 7.51 (2H, m, *ArH*), 3.12 (4H, br.s, *PCH*), 2.90 – 2.80 (4H, m, *CH*₂), 2.50 – 2.37 (4H, m, *CH*₂), 2.36 – 2.18 (2H, m, *CH*₂), 2.14 – 1.92 (12H, m, *CH*₂) and 1.85 – 1.75 (2H, m, *CH*₂) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_2Cl_2): δ 133.3 (d, $J = 17$ Hz), 131.7, 31.8, 31.5, 31.4, 29.1 (t, $J = 3$ Hz), 21.2, 21.2, 21.1 and 19.5 (t, $J = 3$ Hz). ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2): δ 38.6 ppm. HR-MS (+ve ESI): *m/z* calculated for $\text{C}_{22}\text{H}_{32}\text{Cl}_2\text{NaP}_2\text{Pd}^+$, $[\text{M}+\text{Na}]^+$ 557.0283 required; 557.0287 found. Elem. Anal. Calcd for $\text{C}_{22}\text{H}_{32}\text{Cl}_2\text{P}_2\text{Pd}\cdot\text{CH}_2\text{Cl}_2$: C, 44.51; H, 5.52. Found: C, 44.22; H, 5.45.



(1,2-Di(9-phosphabicyclo[4.2.1]nonan-9-yl)benzene)dichloropalladium(II) complex, $[\text{Pd}(\text{L6})\text{Cl}_2]$ Synthesized via the general procedure for synthesis of $\text{Pd}(\text{diphosphine})\text{Cl}_2$ complexes, precipitated with hexane instead of cyclohexane. Diphosphine = 1,2-di(9-phosphabicyclo[4.2.1]nonan-9-yl)benzene (**L6**). ^1H NMR (400 MHz, CDCl_3): δ 7.73 – 7.67 (2H, m, *ArH*), 7.55 – 7.50 (2H, m, *ArH*), 4.26 – 4.16 (4H, m, *PCH*), 2.26 – 2.14 (1H, m), 1.98 – 1.85 (1H, m), 1.76 – 1.61 (4H, m), 1.61 – 1.51 (2H, m), 1.49 – 1.33 (10H, m) and 0.96 – 0.90 ppm (6H, m). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 131.0, 129.0, 68.3, 38.9, 30.5, 29.1, 23.9, 23.1, 14.2 and 11.1 ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ 65.1 ppm. HR-MS (+ve ESI): *m/z* calculated for $\text{C}_{22}\text{H}_{32}\text{Cl}_2\text{NaP}_2\text{Pd}^+$, $[\text{M}+\text{Na}]^+$ 557.0283 required; 557.0292 found. Elem. Anal. Calcd for $\text{C}_{22}\text{H}_{32}\text{Cl}_2\text{P}_2\text{Pd}$: C, 49.32; H, 6.02. Found: C, 55.96; H, 7.96. This compound contains n-hexane, used during workup, which could not be removed after prolonged exposure to high vacuum. Calcd for $(\text{C}_{22}\text{H}_{32}\text{Cl}_2\text{P}_2\text{Pd})(\text{C}_6\text{H}_{14})_{1.4}$: C, 55.73; H, 7.96. The presence of n-hexane is also seen in the ^1H NMR spectrum (Figure S24).



(1,2-di(9-phosphabicyclo[3.3.1]nonan-9-yl)ethane)(μ -chloro)palladium(II) complex, $[\text{Pd}_2(\text{BCOPE})_2(\mu\text{-Cl})_2](\text{O}_3\text{SCH}_3)_2$ The addition of one equivalent of $\text{Ag}(\text{O}_3\text{SCH}_3)$ to a solution of $[\text{Pd}(\text{BCOPE})\text{Cl}_2]$ in CDCl_3 ($^{31}\text{P}\{^1\text{H}\}$)

NMR (162 MHz, CD₂Cl₂): δ 51.3 ppm) resulted in the formation of a new signal (³¹P {¹H} NMR (162 MHz, CD₂Cl₂): δ 71.4 ppm), upon which a complex slowly crystallized which was identified by XRD analysis as [Pd₂(BCOPE)₂(μ-Cl)₂](O₃SCH₃)₂.

NMR Spectra

¹H NMR (CDCl₃, 400 MHz)

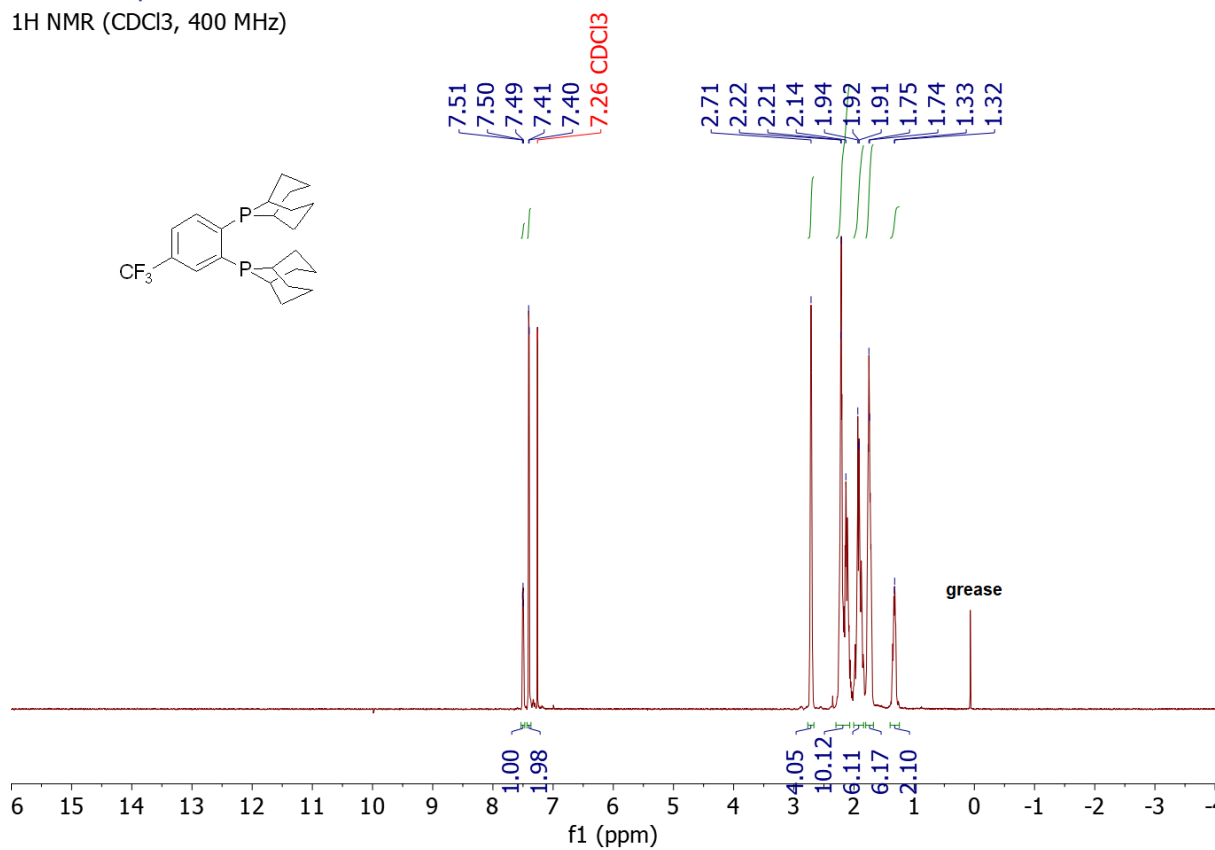


Figure S1. ¹H NMR (400 MHz, CDCl₃, 25°C) spectrum of 9,9'-(4-(trifluoromethyl)-1,2-phenylene)bis(9-phosphabicyclo[3.3.1]nonane), **Li**.

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz)

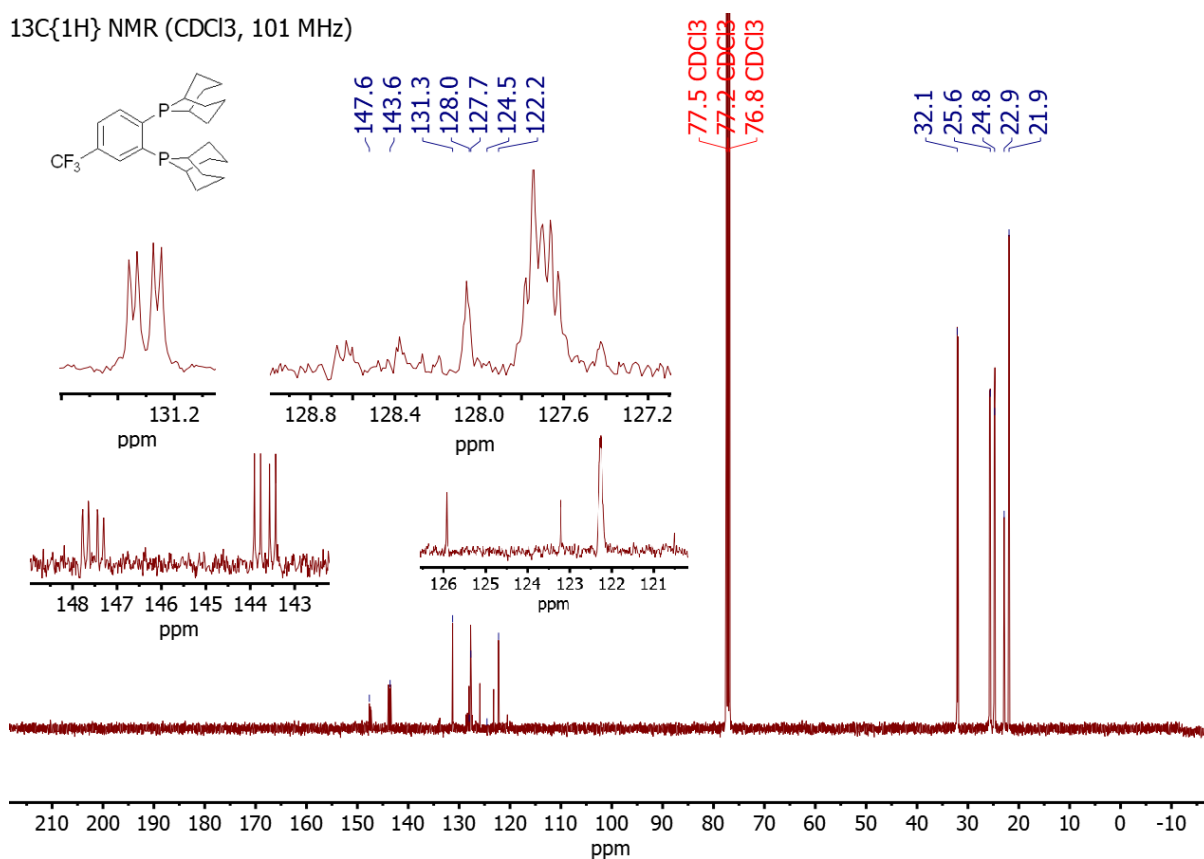


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3 , 25°C) spectrum of 9,9'-(4-(trifluoromethyl)-1,2-phenylene)bis(9-phosphabicyclo[3.3.1]nonane), **1**.

$^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz)

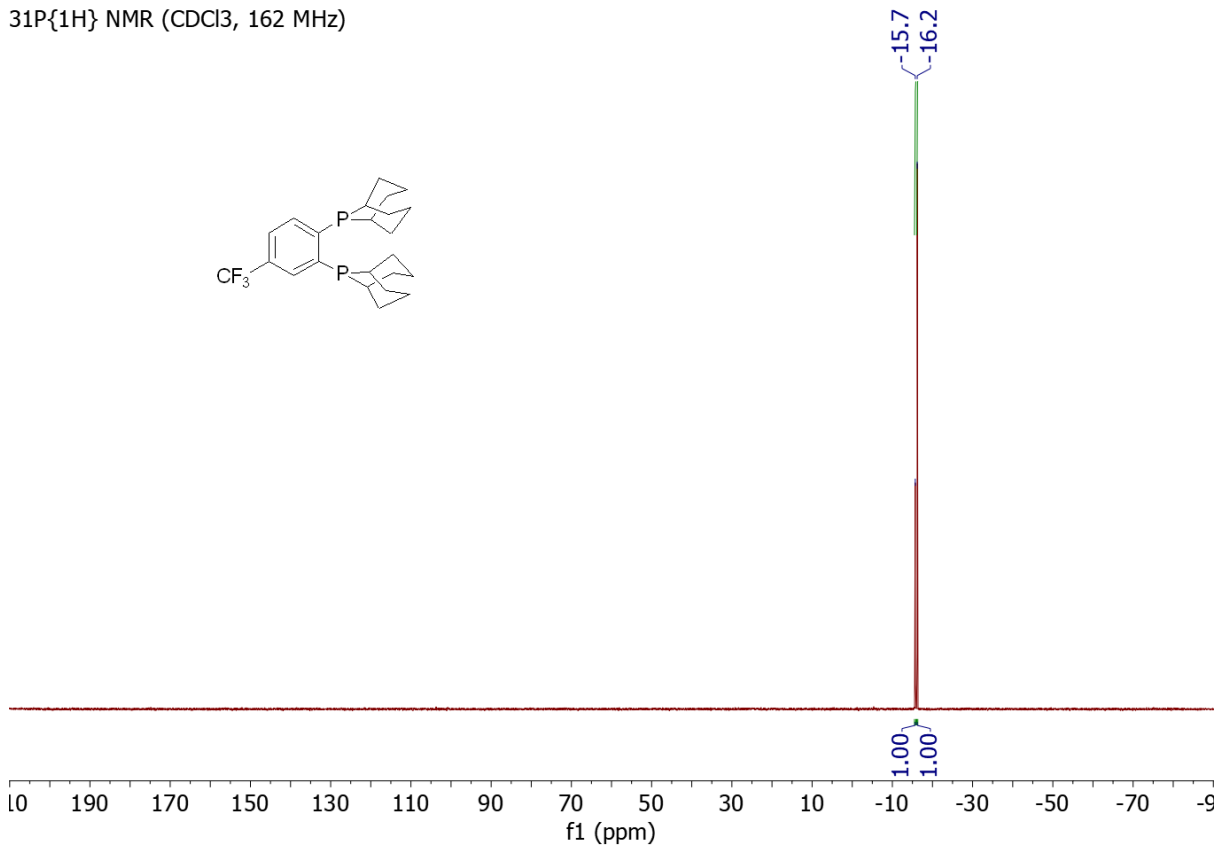


Figure S3. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3 , 25°C) spectrum of 9,9'-(4-(trifluoromethyl)-1,2-phenylene)bis(9-phosphabicyclo[3.3.1]nonane), **1**.

^{19}F NMR (CDCl_3 , 376 MHz)

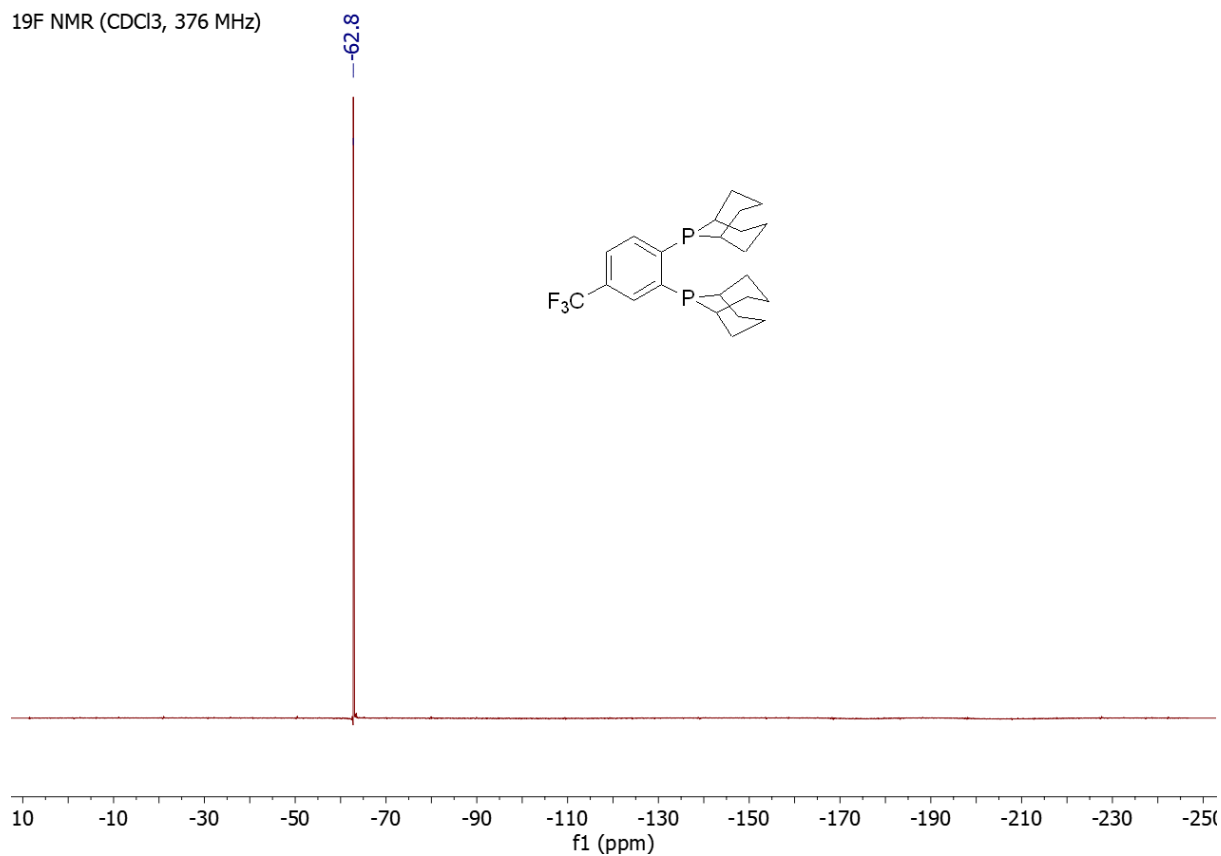


Figure S4. ^{19}F NMR (376 MHz, CDCl_3 , 25°C) spectrum of 9,9'-(4-(trifluoromethyl)-1,2-phenylene)bis(9-phospha-bicyclo[3.3.1]nonane), **L1**.

^1H NMR (CDCl_3 , 400 MHz)

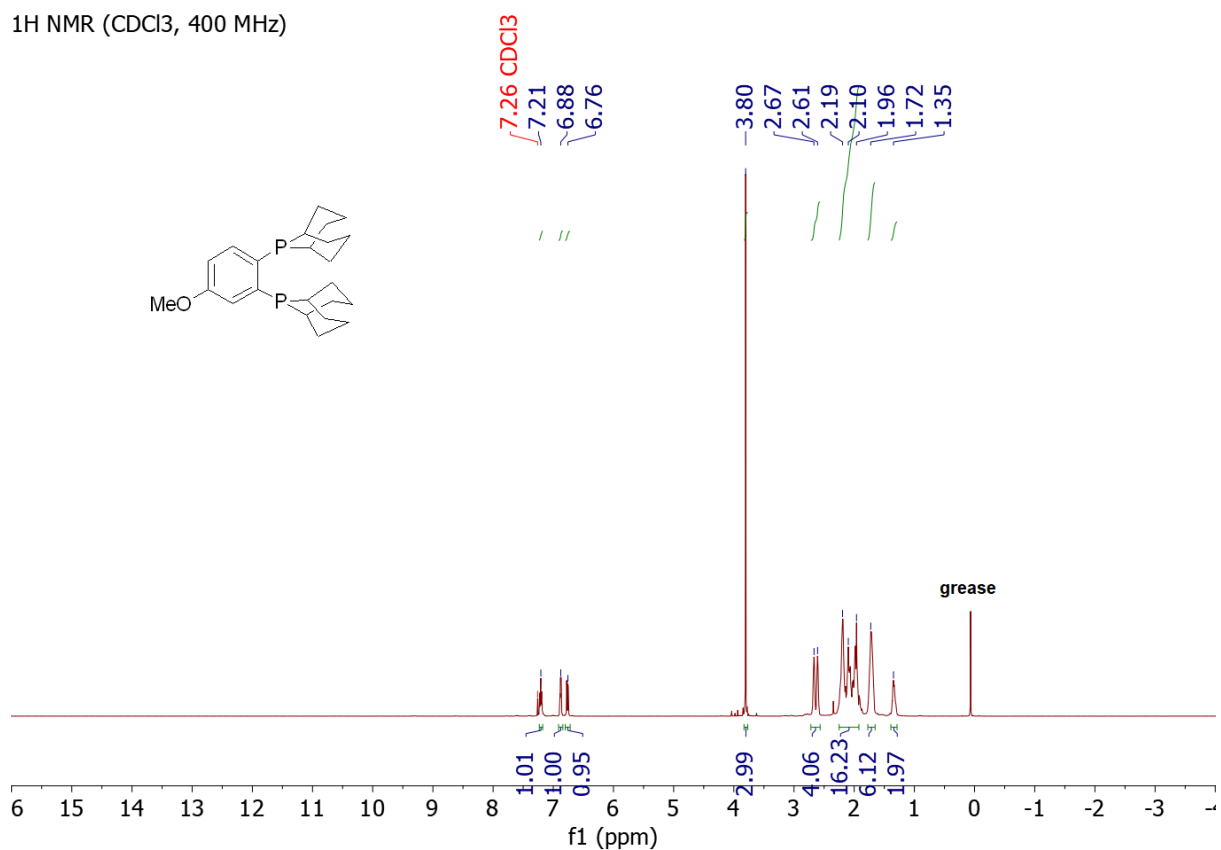


Figure S5. ^1H NMR (400 MHz, CDCl_3 , 25°C) spectrum of 9,9'-(4-methoxy-1,2-phenylene)bis(9-phospha-bicyclo[3.3.1]nonane), **L3**.

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz)

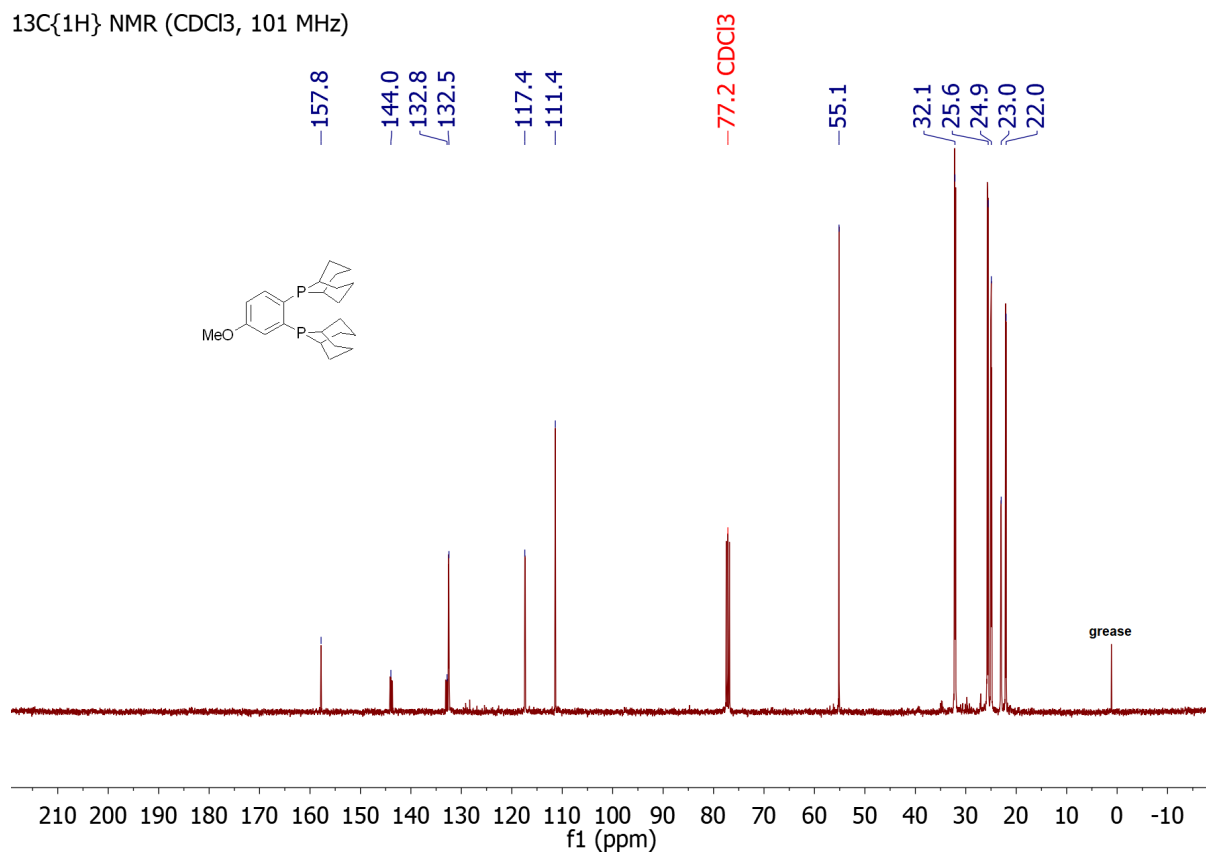


Figure S6. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3 , 25°C) spectrum of 9,9'-(4-methoxy-1,2-phenylene)bis(9-phosphabicyclo[3.3.1]nonane), **L3**.

$^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz)

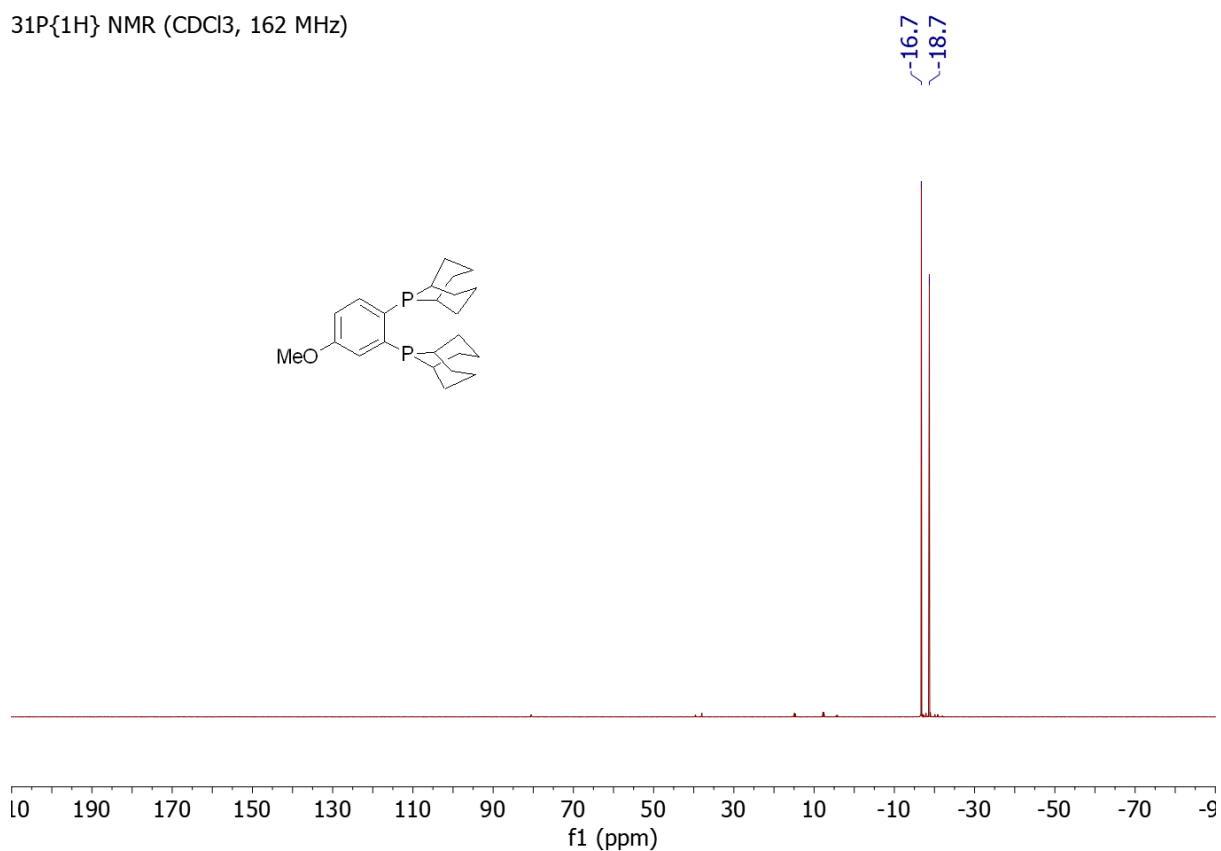


Figure S7. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3 , 25°C) spectrum of 9,9'-(4-methoxy-1,2-phenylene)bis(9-phosphabicyclo[3.3.1]nonane), **L3**.

^1H NMR (CDCl_3 , 400 MHz)

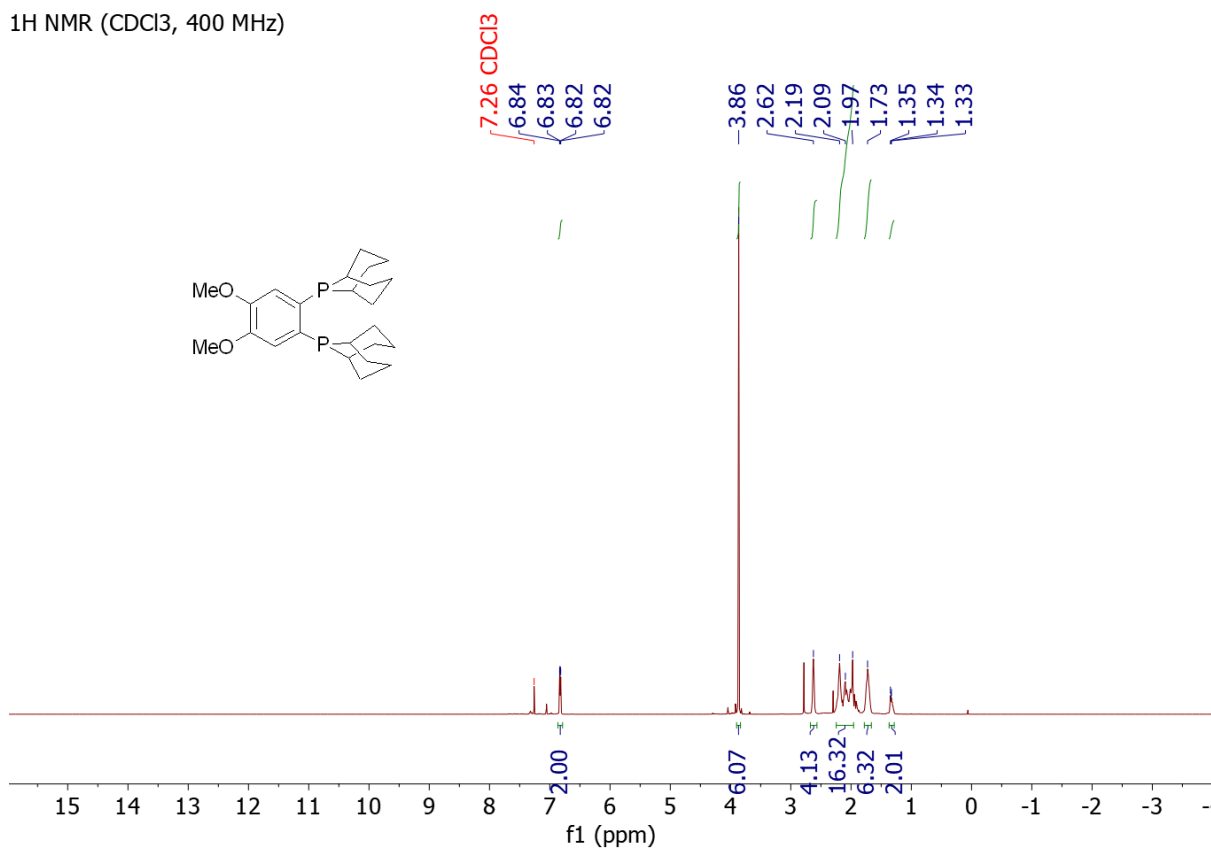


Figure S8. ^1H NMR (400 MHz, CDCl_3 , 25°C) spectrum of 9,9'-(4,5-dimethoxy-1,2-phenylene)bis(9-phosphabicyclo[3.3.1]nonane), **L4**.

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz)

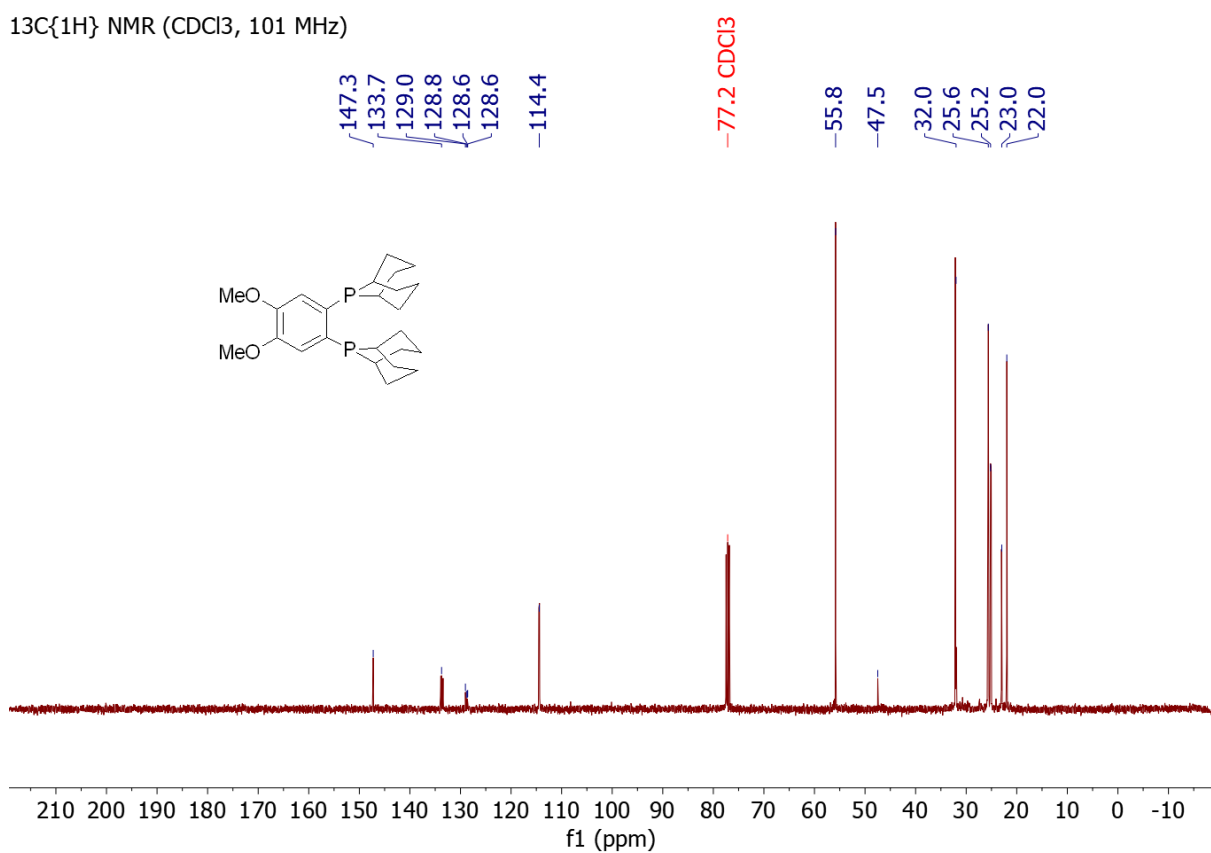


Figure S9. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3 , 25°C) spectrum of 9,9'-(4,5-dimethoxy-1,2-phenylene)bis(9-phosphabicyclo[3.3.1]nonane), **L4**.

$^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz)

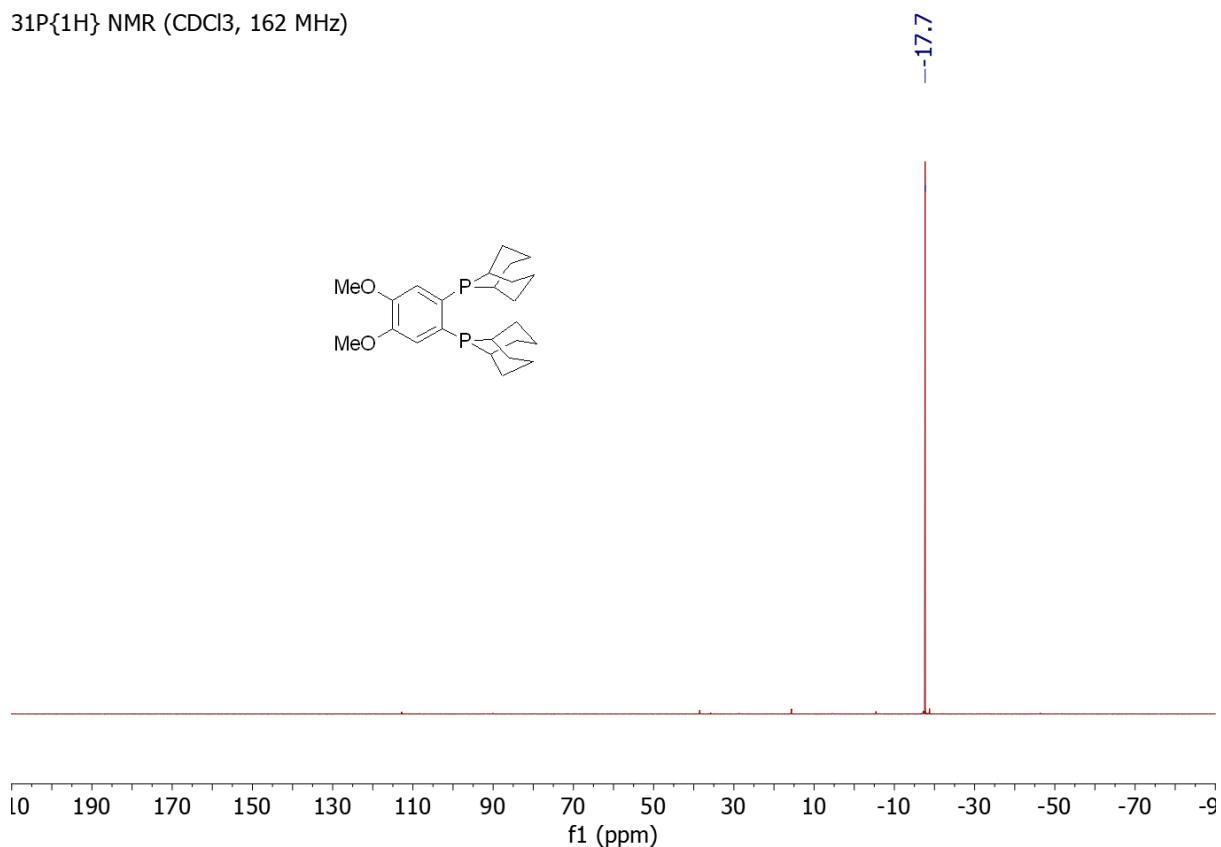


Figure S10. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3 , 25°C) spectrum of 9,9'-(4,5-dimethoxy-1,2-phenylene)bis(9-phosphabicyclo[3.3.1]nonane), **L4**.

^1H NMR (CDCl_3 , 400 MHz)

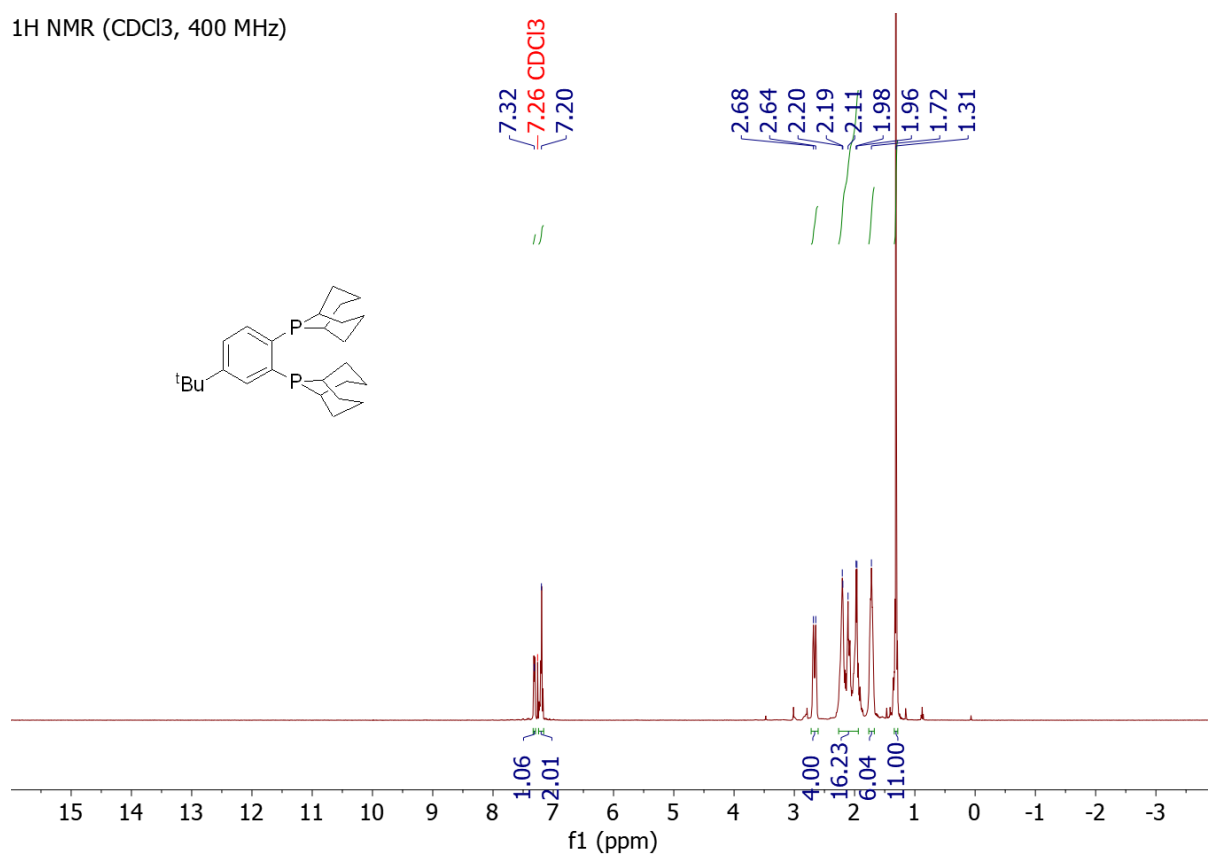


Figure S11. ^1H NMR (400 MHz, CDCl_3 , 25°C) spectrum of 9,9'-(4-(tert-butyl)-1,2-phenylene)bis(9-phosphabicyclo[3.3.1]nonane), **L5**.

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz)

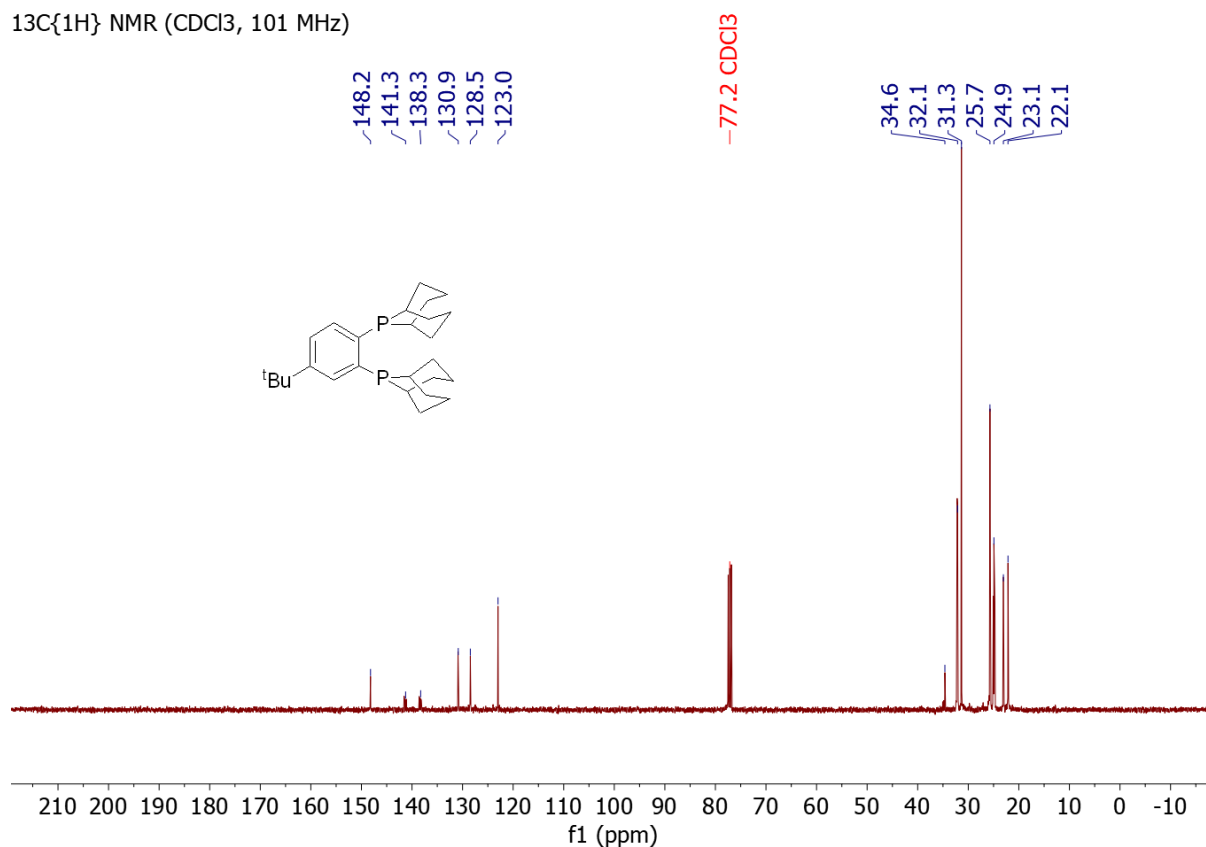


Figure S12. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3 , 25°C) spectrum of 9,9'-(4-(tert-butyl)-1,2-phenylene)bis(9-phosphabicyclo[3.3.1]nonane), **L5**.

$^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz)

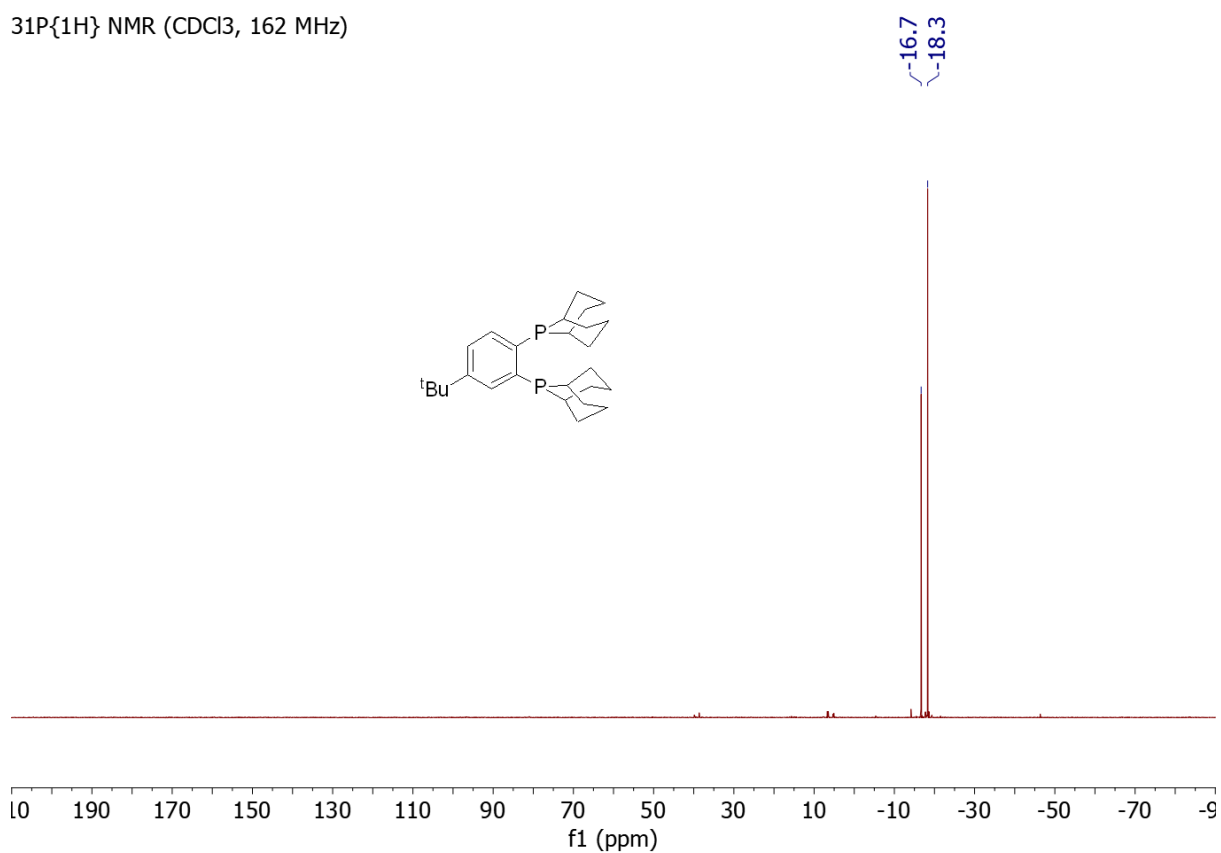


Figure S13. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3 , 25°C) spectrum of 9,9'-(4-(tert-butyl)-1,2-phenylene)bis(9-phosphabicyclo[3.3.1]nonane), **L5**.

^1H NMR (CDCl_3 , 400 MHz)

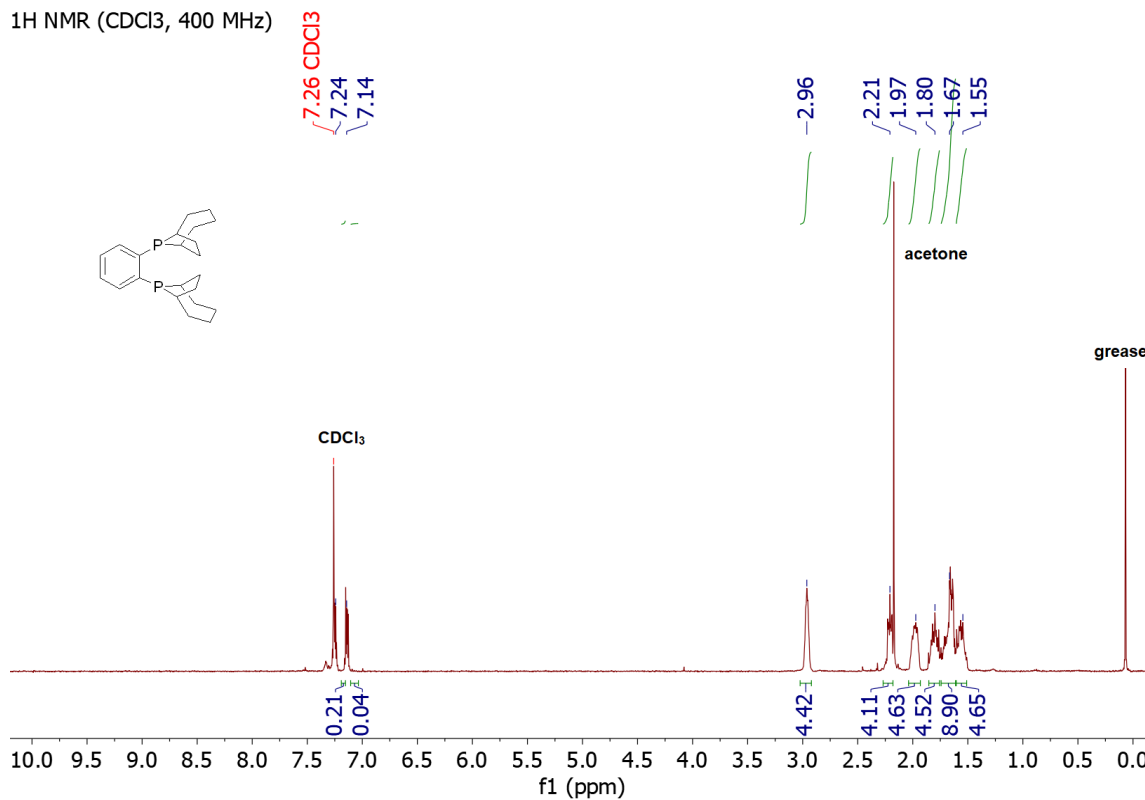


Figure S14. ^1H NMR (400 MHz, CDCl_3 , 25°C) spectrum of 1,2-di(9-phosphabicyclo[4.2.1]nonan-9-yl)benzene, L6.

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz)

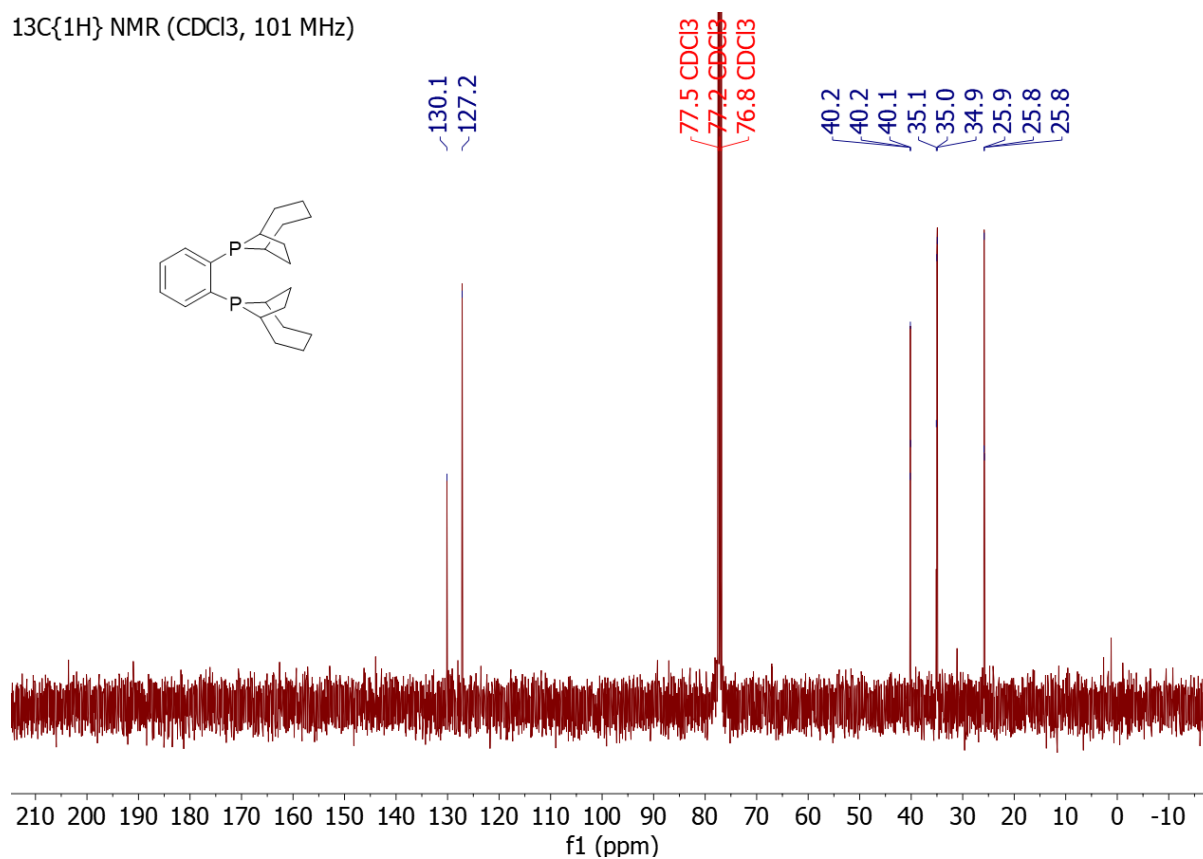


Figure S15. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3 , 25°C) spectrum of 1,2-di(9-phosphabicyclo[4.2.1]nonan-9-yl)benzene, L6.

$^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz)

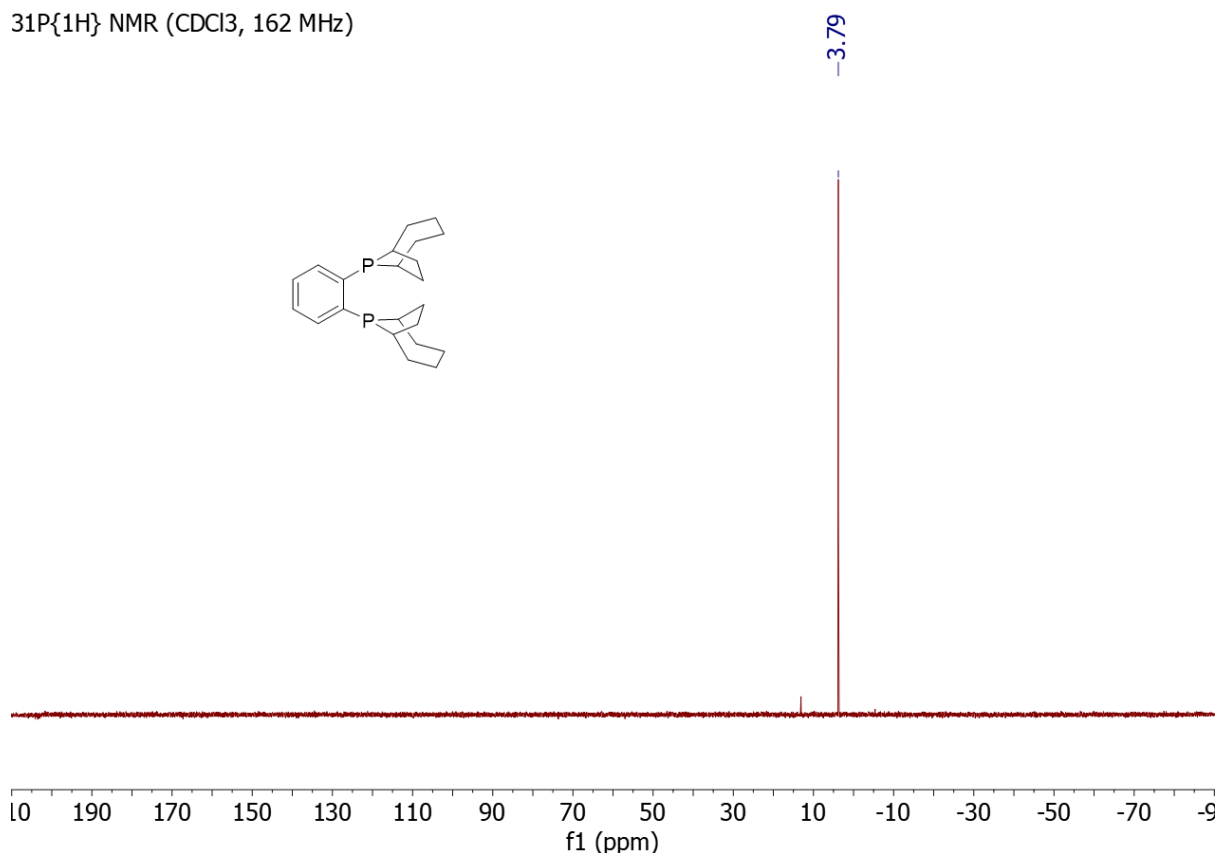


Figure S16. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3 , 25°C) spectrum of 1,2-di(9-phoshabicyclo[4.2.1]nonan-9-yl)benzene, L6.

^1H NMR (CD_2Cl_2 , 400 MHz)

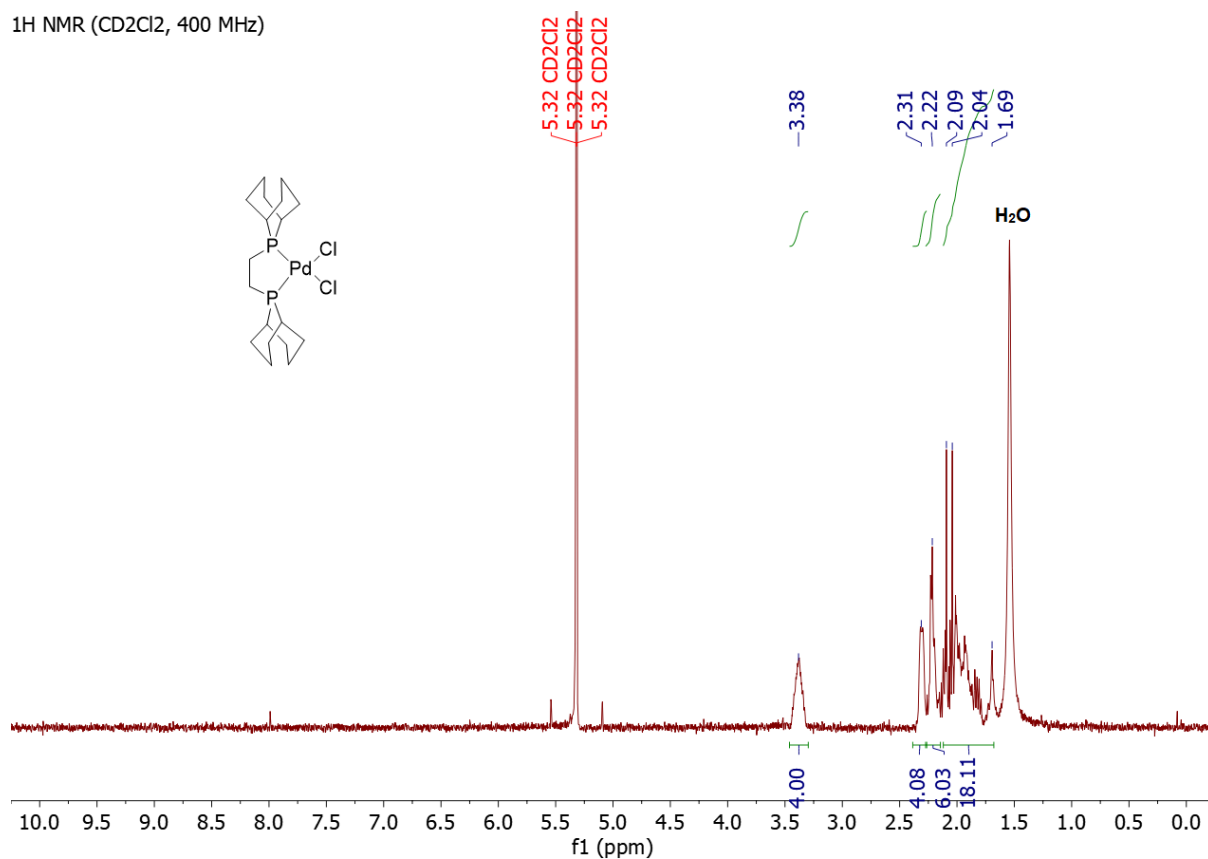


Figure S17. ^1H NMR (400 MHz, CD_2Cl_2 , 25°C) spectrum of (1,2-di(9-phoshabicyclo[3.3.1]nonan-9-yl)ethane)dichloropalladium(II) complex, $[\text{Pd}(\text{BCOPE})\text{Cl}_2]$.

$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 101 MHz)

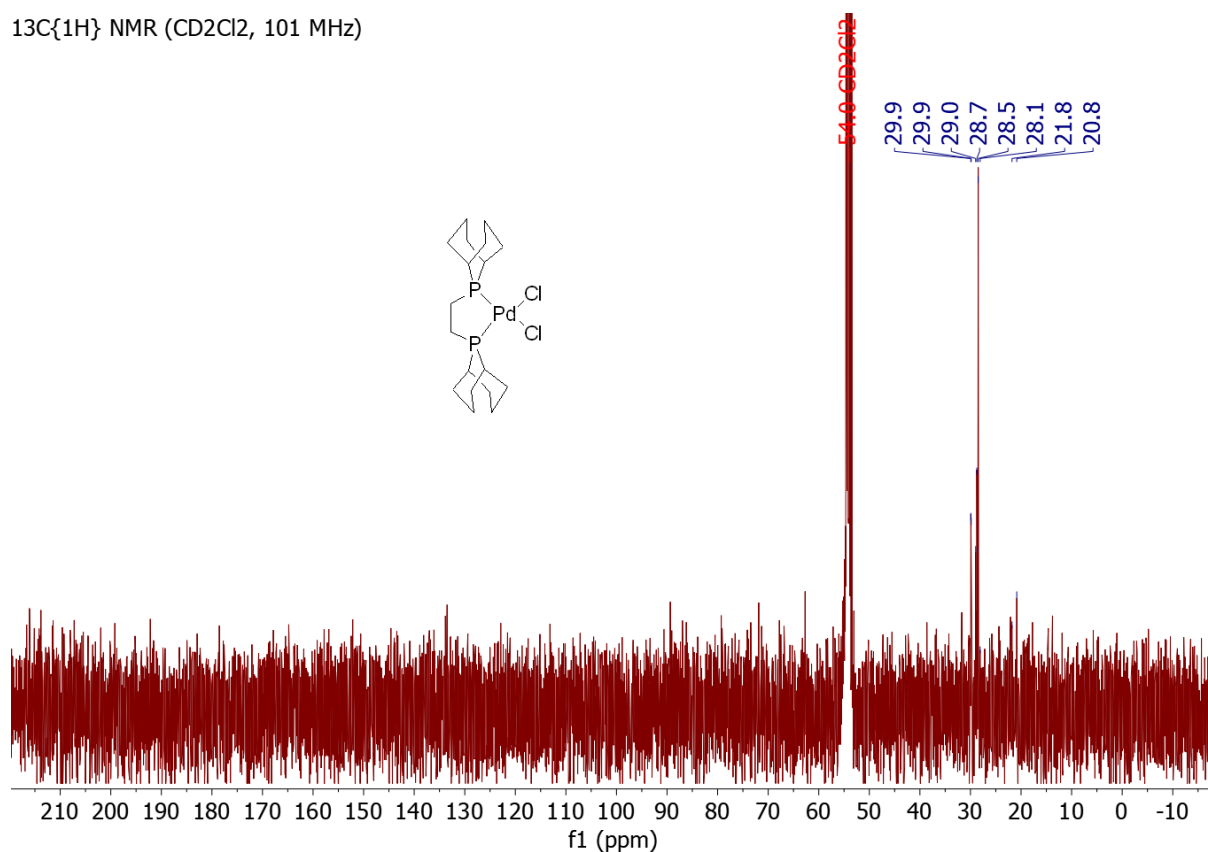


Figure S18. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_2Cl_2 , 25°C) spectrum of (1,2-di(9-phosphabicyclo[3.3.1]nonan-9-yl)ethane)dichloropalladium(II) complex, $[\text{Pd}(\text{BCOPE})\text{Cl}_2]$.

$^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 162 MHz)

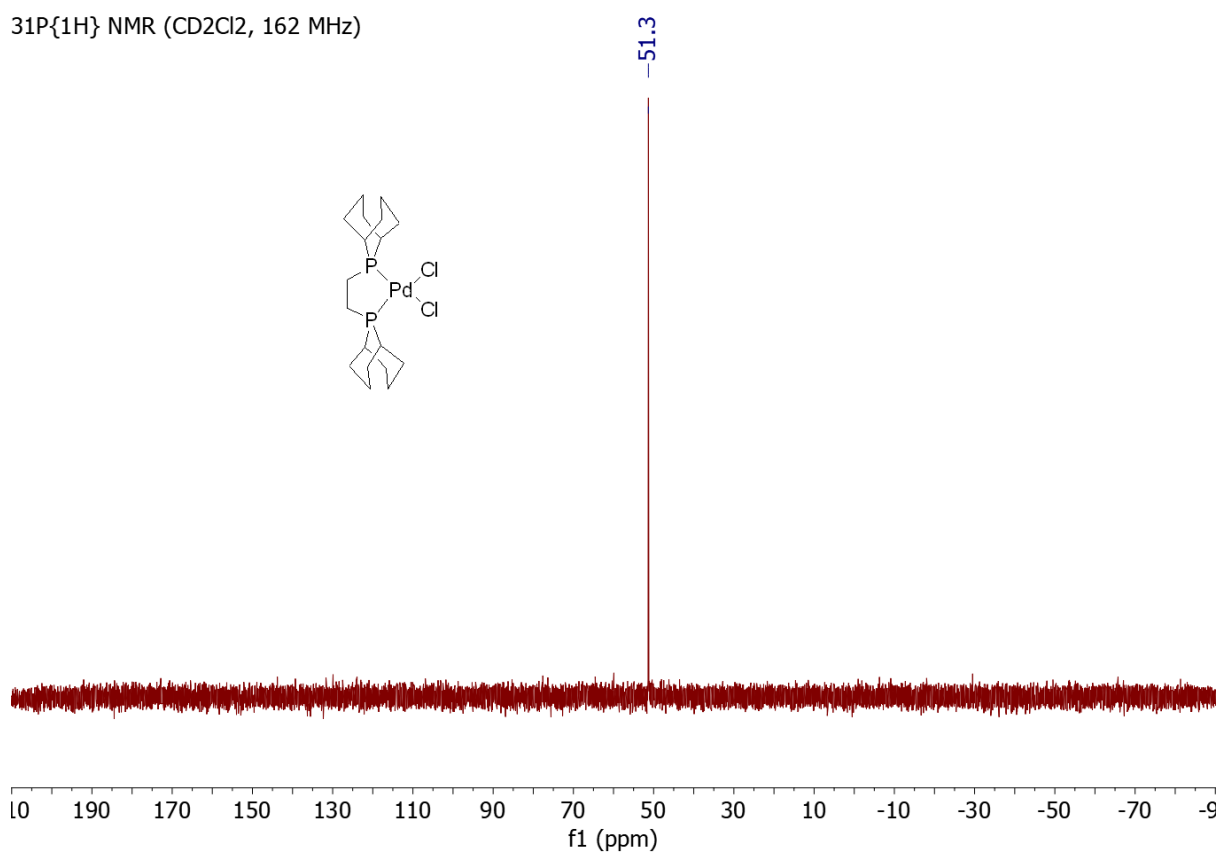
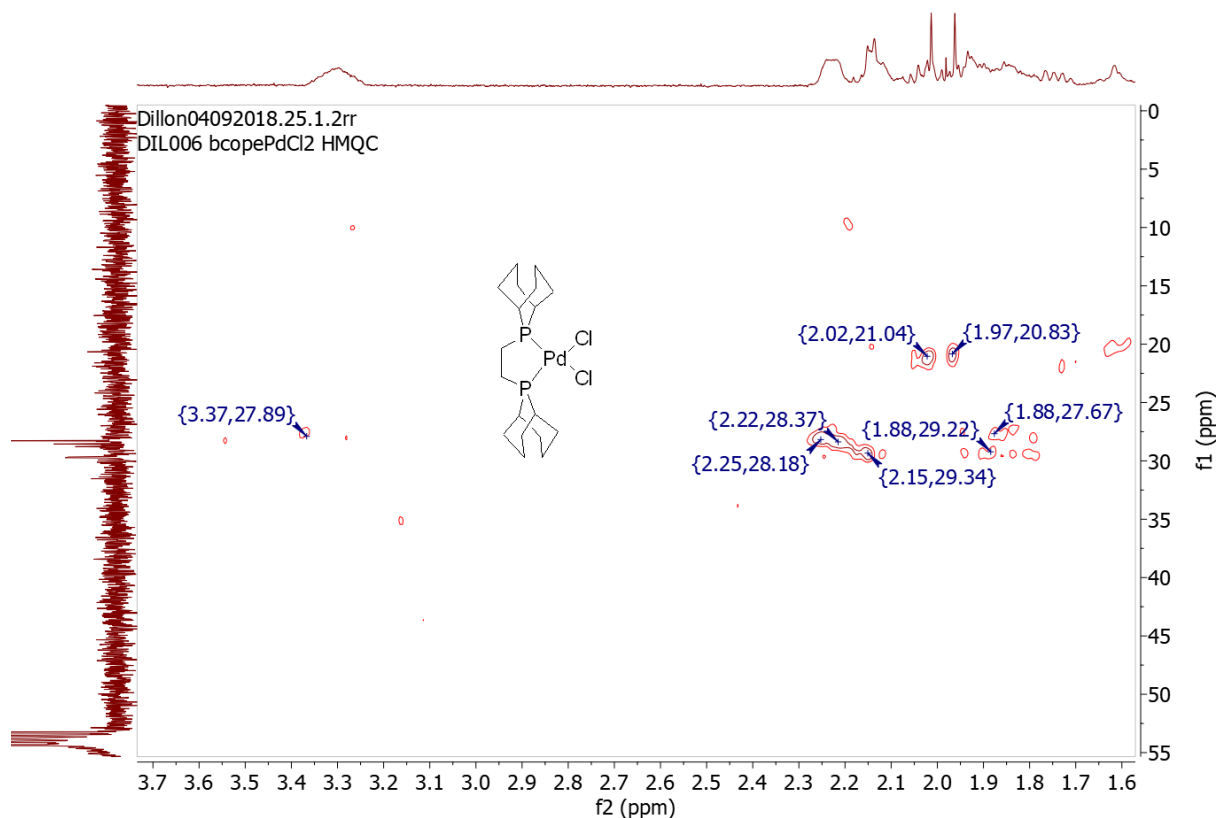
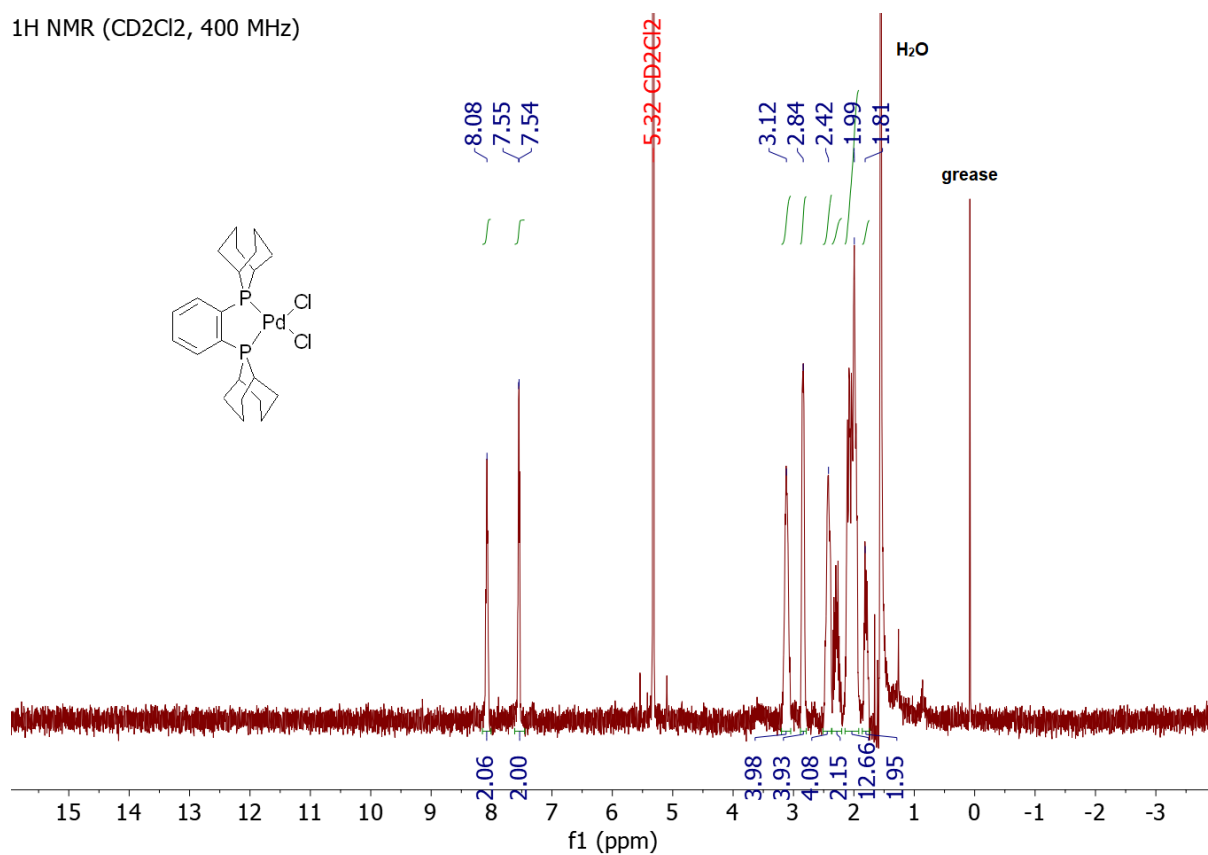


Figure S19. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2 , 25°C) spectrum of (1,2-di(9-phosphabicyclo[3.3.1]nonan-9-yl)ethane)dichloropalladium(II) complex, $[\text{Pd}(\text{BCOPE})\text{Cl}_2]$.



^1H NMR (CD_2Cl_2 , 400 MHz)



$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 101 MHz)

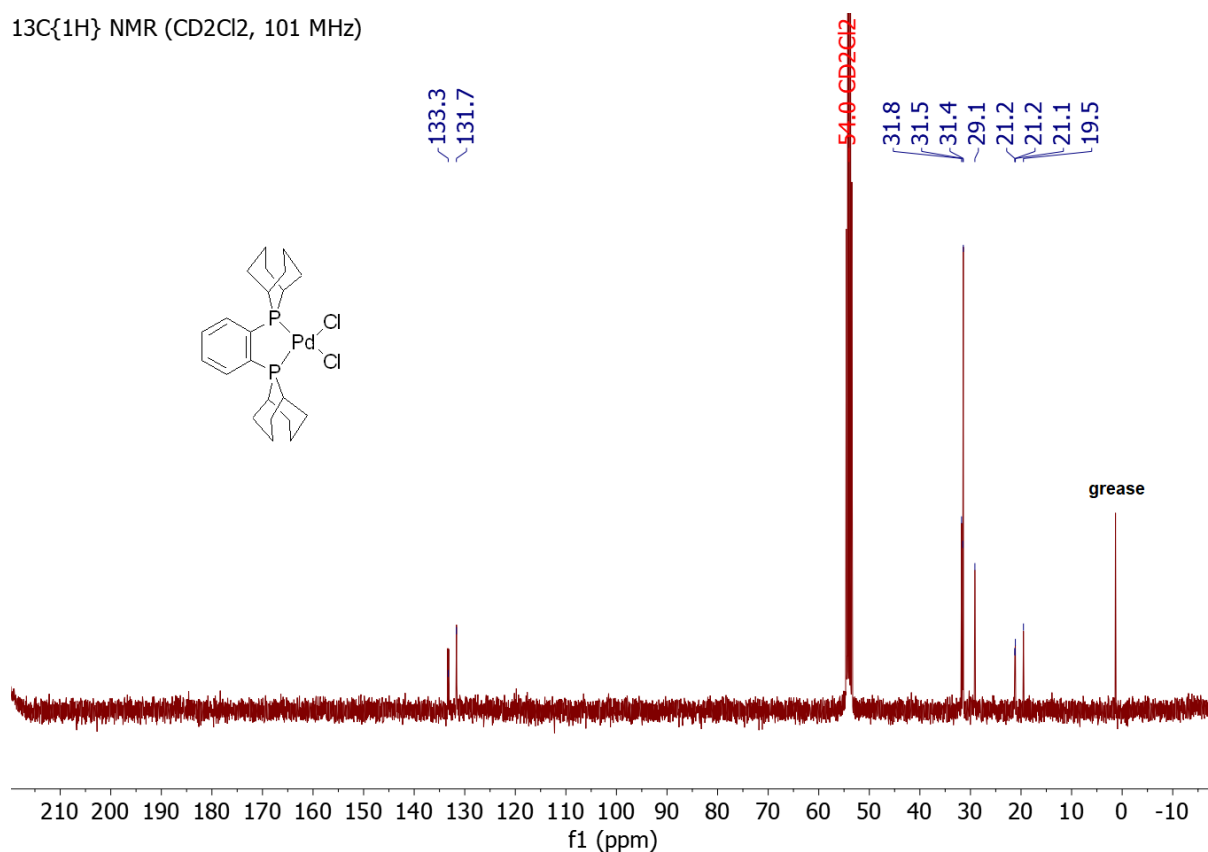


Figure S22. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_2Cl_2 , 25°C) spectrum of (1,2-di(9-phosphabicyclo[3.3.1]nonan-9-yl)benzene)dichloropalladium(II) complex, $[\text{Pd}(\text{L}_2)\text{Cl}_2]$.

$^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 162 MHz)

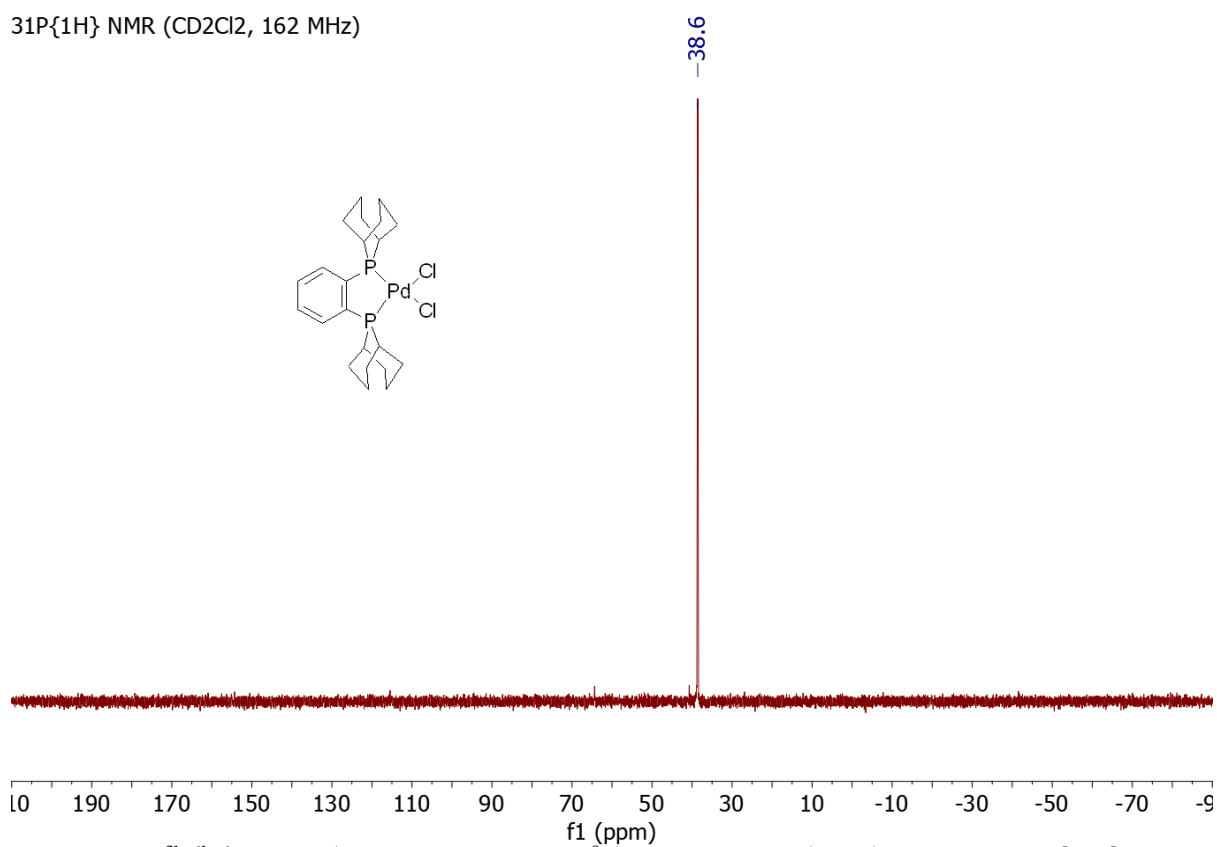


Figure S23. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2 , 25°C) spectrum of (1,2-di(9-phosphabicyclo[3.3.1]nonan-9-yl)benzene)dichloropalladium(II) complex, $[\text{Pd}(\text{L}_2)\text{Cl}_2]$.

^1H NMR (CDCl_3 , 400 MHz)

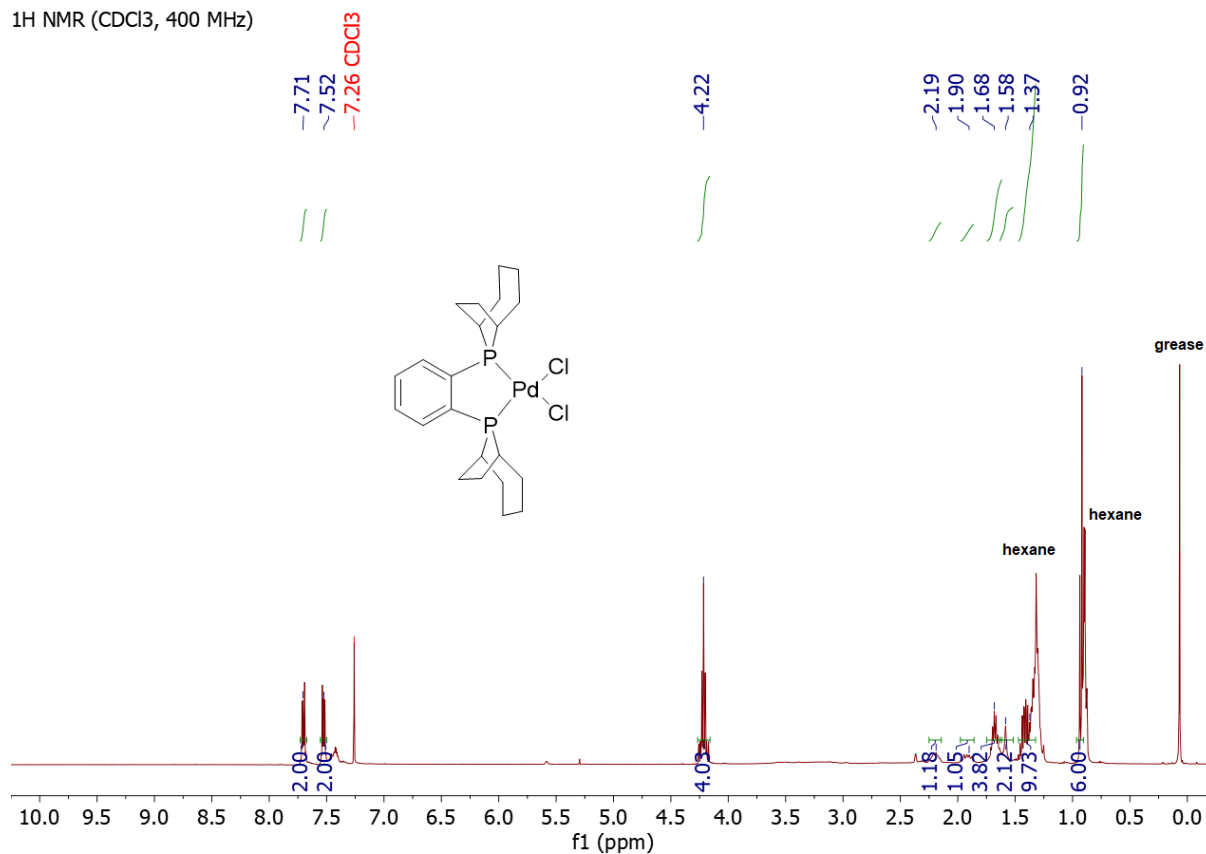


Figure S24. ^1H NMR (400 MHz, CDCl_3 , 25°C) spectrum of (1,2-Di(9-phosphabicyclo[4.2.1]nonan-9-yl)benzene)dichloropalladium(II) complex, $[\text{Pd}(\text{L6})\text{Cl}_2]$.

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz)

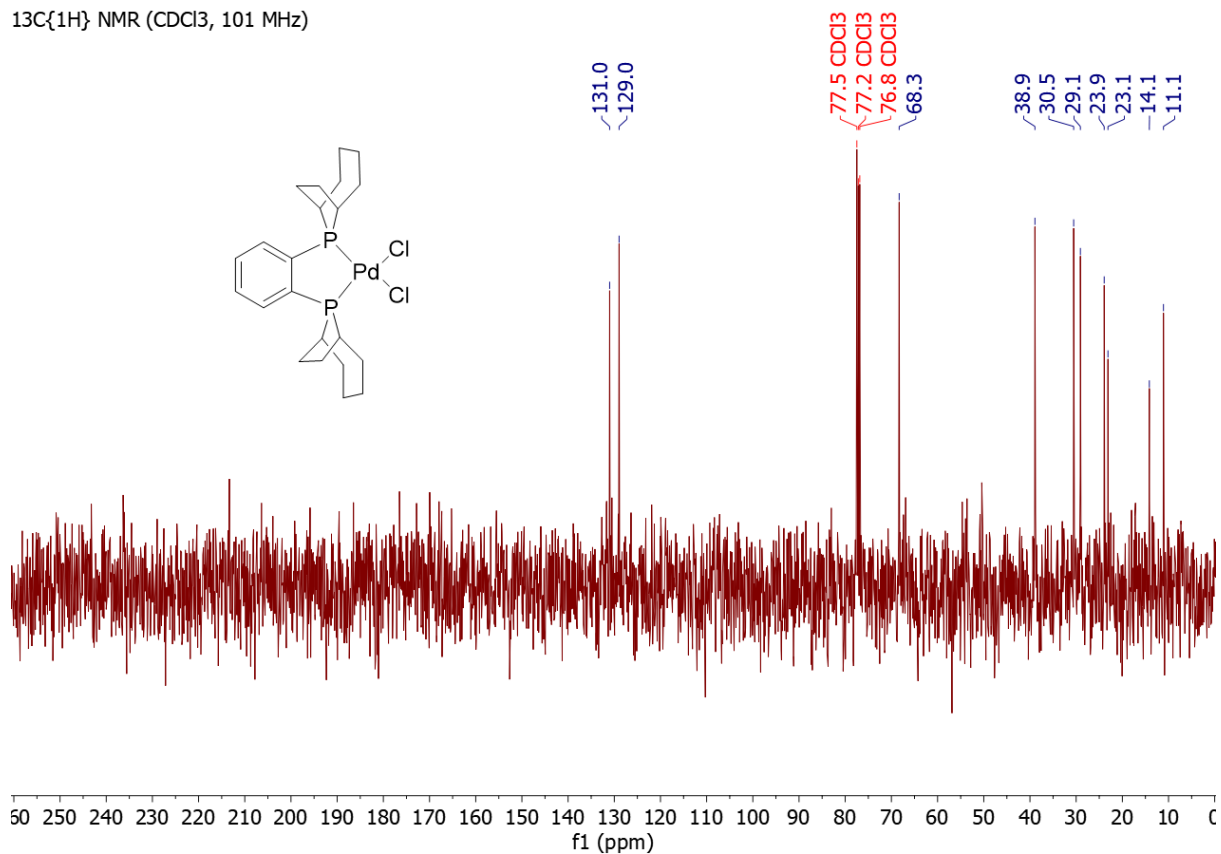


Figure S25. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3 , 25°C) spectrum of (1,2-Di(9-phosphabicyclo[4.2.1]nonan-9-yl)benzene)dichloropalladium(II) complex, $[\text{Pd}(\text{L6})\text{Cl}_2]$.

$^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz)

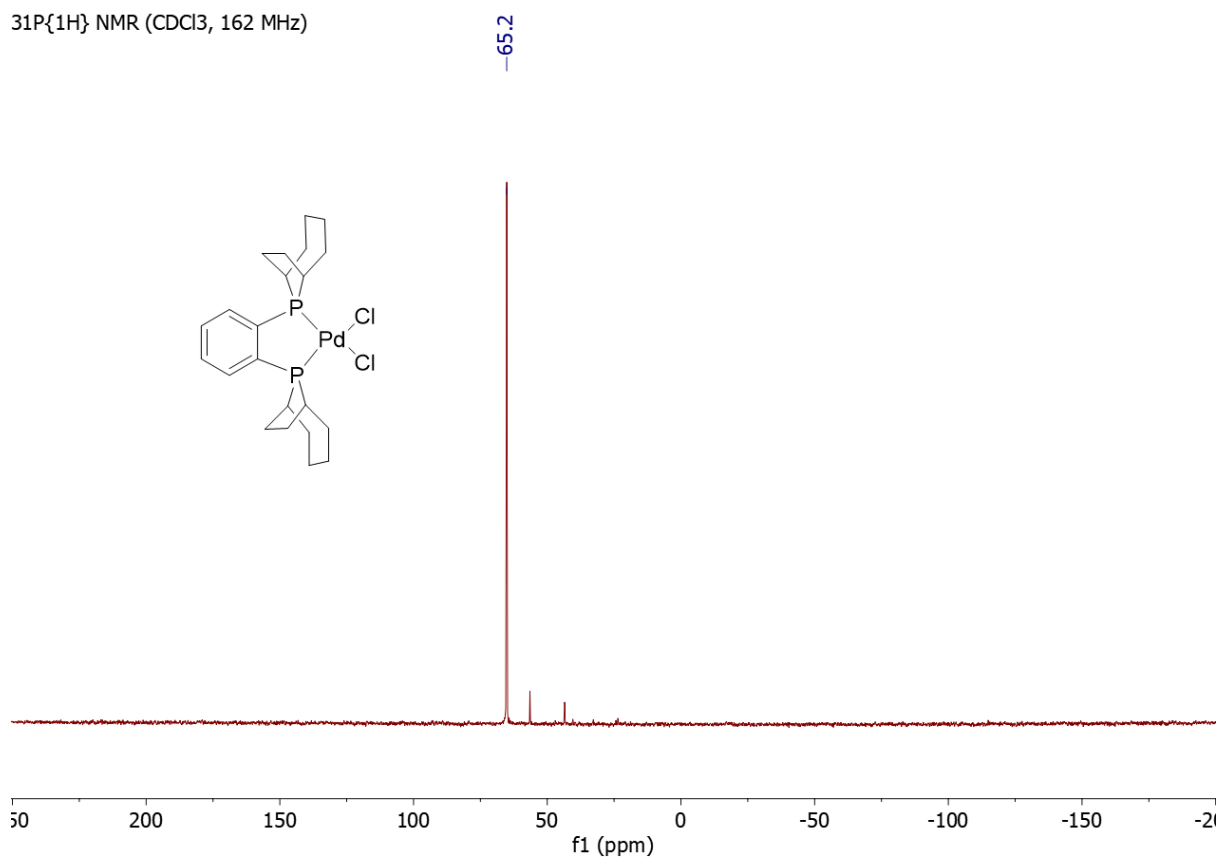


Figure S26. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3 , 25°C) spectrum of (1,2-Di(9-phospha-bicyclo[4.2.1]nonan-9-yl)benzene)dichloropalladium(II) complex, $[\text{Pd}(\text{L6})\text{Cl}_2]$.

Ligand Buried Volume (%V_Bur)

[Pd(**BCOPE**)Cl₂] and [Pd(**L2**)Cl₂] structures obtained from XRD were subjected to ligand buried volume calculations using SambVca 2.1.^{4,5} The Pd atom was set as the coordination centre, the P donor atoms were selected for z-axis definition (z-negative) and the C₂-bridge selected for xz-plane definition. The Pd and Cl atoms were deleted to leave only the ligand of interest for buried volume calculation. Atomic radii were set at Bondi radii and sphere radius set to 3.5 Å. Mesh spacing for numerical integration set to 0.10 Å and hydrogen atoms were omitted from the calculation.

[Pd(**BCOPE**)Cl₂]

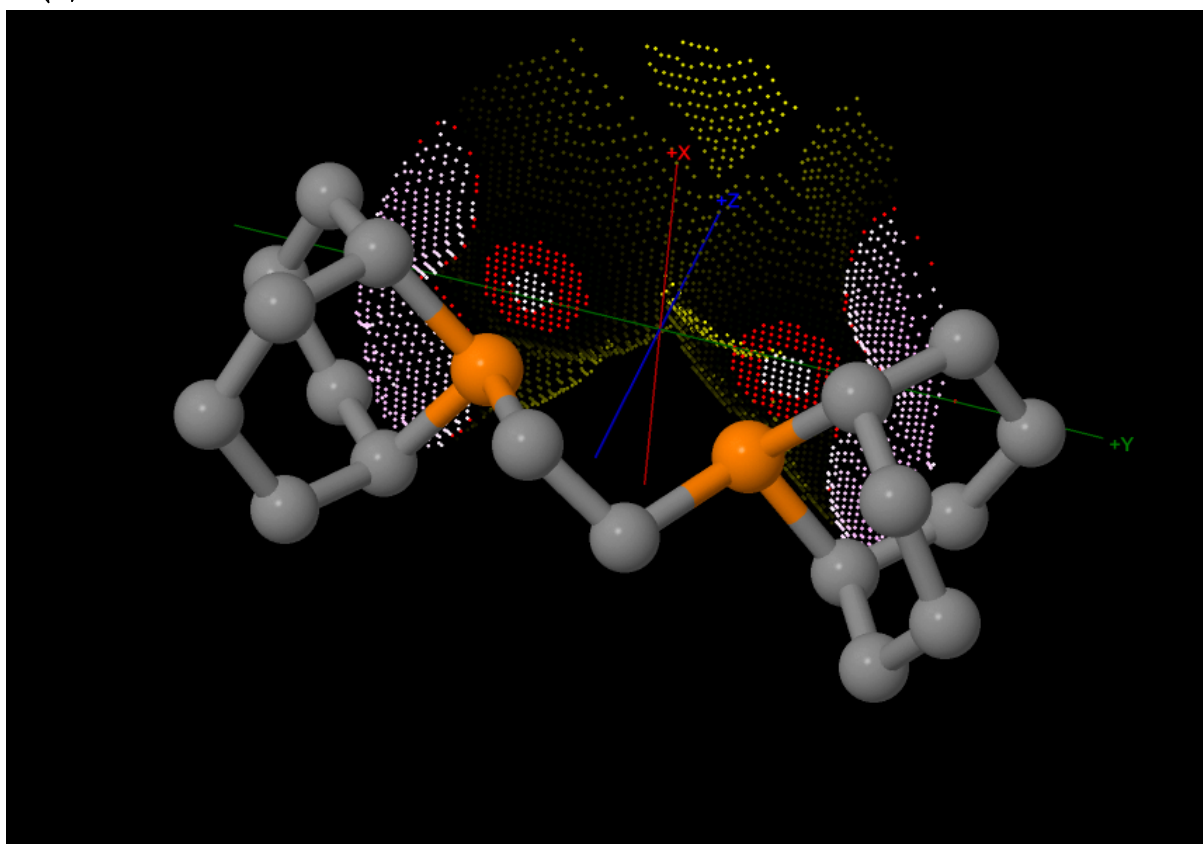
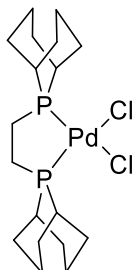


Figure S27. Visual representation of ligand buried volume (%V_Bur) of (1,2-di(9-phospha-bicyclo[3.3.1]nonan-9-yl)ethane)dichloropalladium(II) complex, [Pd(**BCOPE**)Cl₂].

V Free	V Buried	V Total	V Exact
114.4	65.1	179.5	179.6

%V_Free	%V_Bur	% Tot/Ex
63.7	36.3	100.0

Quadrant	V_f	V_b	V_t	%V_f	%V_b
SW	29.6	15.2	44.9	66.1	33.9
NW	27.3	17.6	44.9	60.8	39.2
NE	29.6	15.3	44.8	65.9	34.1
SE	27.9	17.0	44.9	62.2	37.8

Figure S28. Ligand buried volume (%V_Bur) values for (1,2-di(9-phosphabicyclo[3.3.1]nonan-9-yl)ethane)dichloropalladium(II) complex, [Pd(BCOPE)Cl₂].

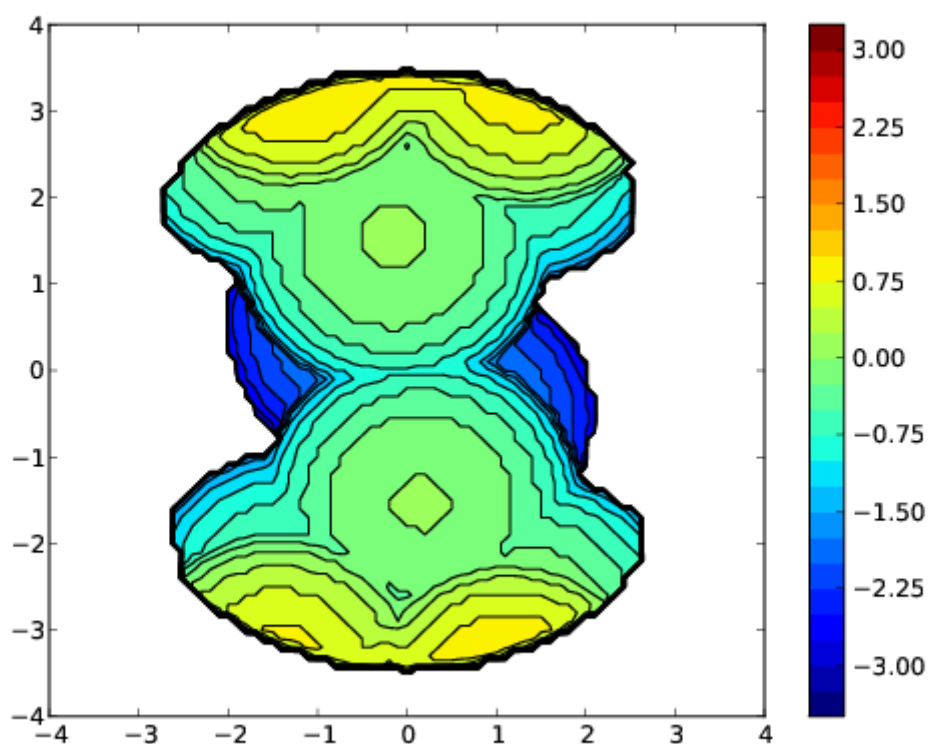


Figure S29. Steric map for (1,2-di(9-phosphabicyclo[3.3.1]nonan-9-yl)ethane)dichloropalladium(II) complex, [Pd(BCOPE)Cl₂].

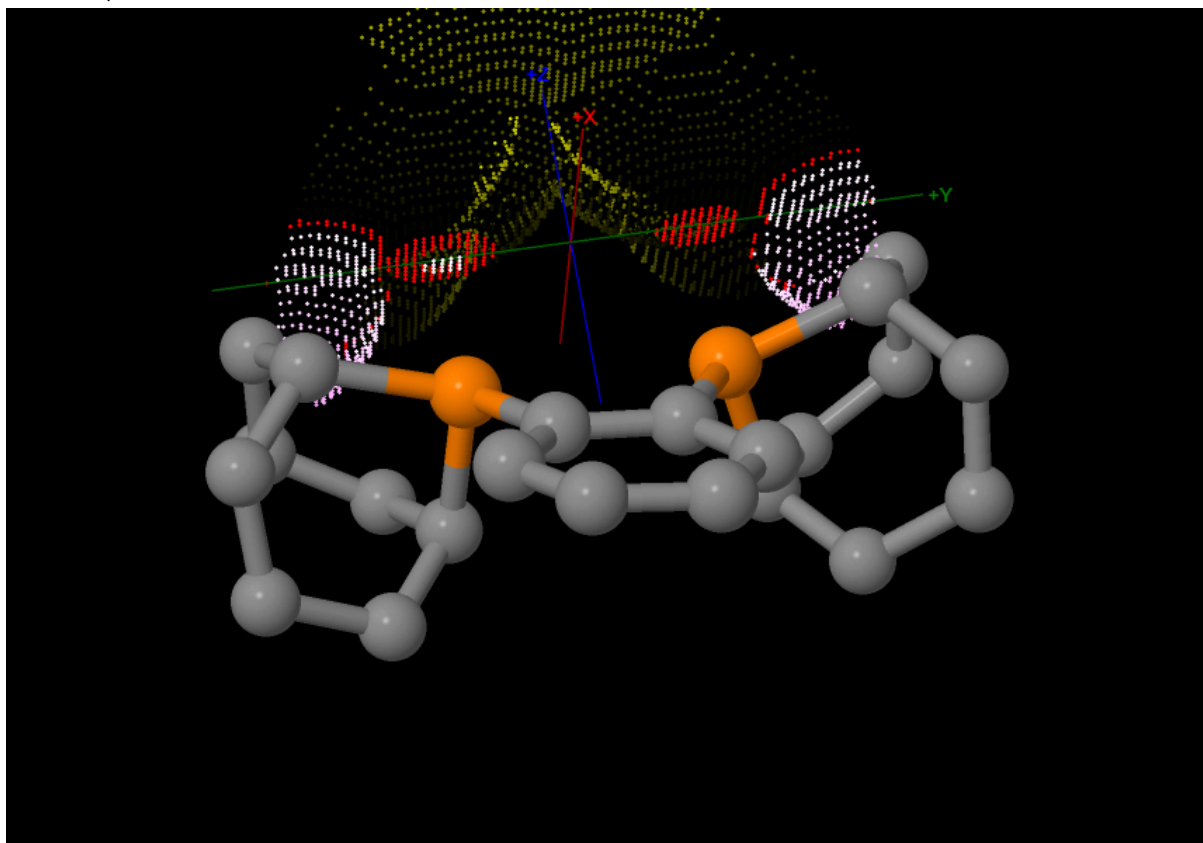
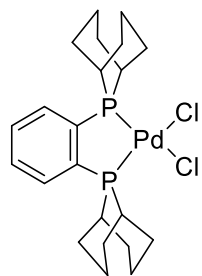
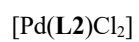


Figure S30. Visual representation of ligand buried volume (%V_Bur) of (1,2-di(9-phospha-bicyclo[3.3.1]nonan-9-yl)benzene)dichloropalladium(II) complex, [Pd(L₂)Cl₂].

V Free	V Buried	V Total	V Exact
112.8	66.7	179.5	179.6

%V_Free	%V_Bur	% Tot/Ex
62.8	37.2	100.0

Quadrant	V_f	V_b	V_t	%V_f	%V_b
SW	27.3	17.5	44.9	60.9	39.1
NW	27.1	17.7	44.9	60.4	39.6
NE	29.8	15.1	44.8	66.4	33.6
SE	28.5	16.4	44.9	63.5	36.5

Figure S31. Ligand buried volume (%V_Bur) values for (1,2-di(9-phosphabicyclo[3.3.1]nonan-9-yl)benzene)dichloropalladium(II) complex, [Pd(L₂)Cl₂].

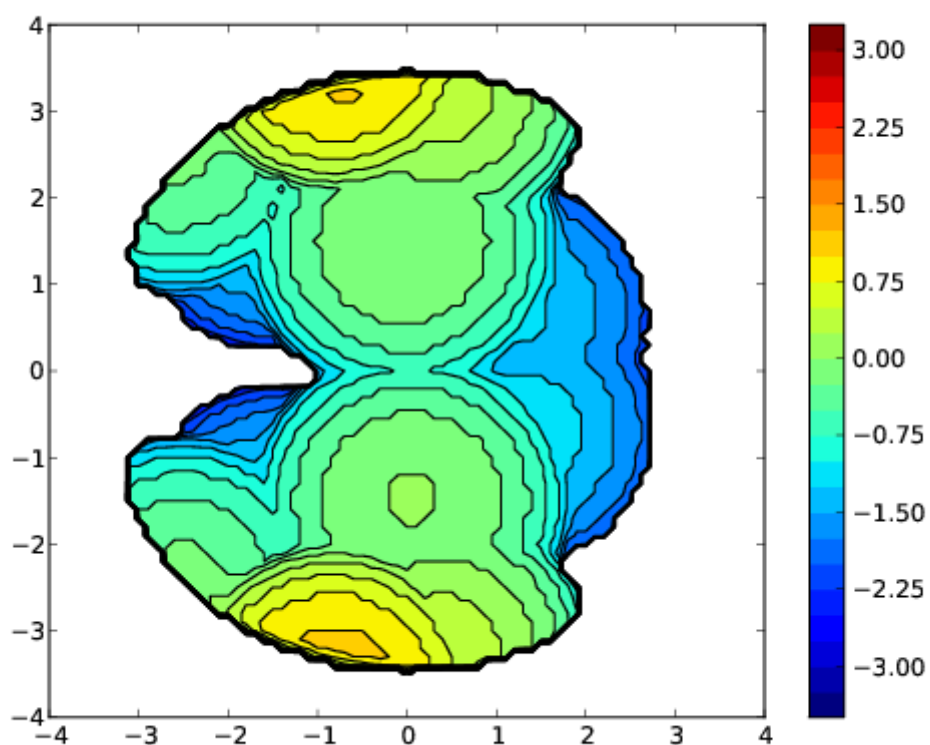


Figure S32. Steric map for (1,2-di(9-phosphabicyclo[3.3.1]nonan-9-yl)benzene)dichloropalladium(II) complex, [Pd(L₂)Cl₂].

Catalysis Procedures

General procedure for Pd-catalyzed alkene hydroformylation (1-hexene and methyl pentenoate)

Hydroformylations were carried out in a 160 mL stainless steel pressure Parr reactor (452HC9) and heated externally with a metal jacket as part of the Parr®5500 series compact reactor system. Prior to a hydroformylation experiment, the reactor was purged 3 times with argon. A schlenk tube equipped with a magnetic stirrer bar was taken into the glovebox and charged sequentially with Pd(OAc)₂ then ligand. A stock solution of acid in reaction solvent followed by aqueous NaCl (if any) was injected into the schlenk tube, and the catalyst mixture stirred for 5 min before it was injected into the Parr reactor under a stream of argon. The schlenk tube was washed with solvent twice and the washes injected into the reactor under a stream of argon. Olefin, then anisole (internal standard) was injected into the Parr reactor before being pressurized with CO to the desired partial pressure and left to stir for 5 min before being pressurized with H₂ to the total desired pressure and sealed. The reactor was stirred at reaction temperature for the desired reaction time before slowly cooling to <10 °C in an ice-water bath. The reactor was then depressurized carefully, and products were characterized by gas chromatography.

General procedure for Pd-catalyzed methoxycarbonylation of 1-octene

Methoxycarbonylations were carried out in a 160 mL stainless steel pressure Parr reactor (452HC9) and heated externally with a metal jacket as part of the Parr®5500 series compact reactor system. Prior to a methoxycarbonylation experiment, the reactor was purged 3 times with argon. A schlenk tube equipped with a magnetic stirrer bar was taken into the glovebox and charged sequentially with Pd(OAc)₂ (0.04 mmol), ligand (0.06 mmol) then. A stock solution of CH₃SO₃H in MeOH (0.8 M, 2 mL) was injected into the schlenk tube and the catalyst mixture stirred for 5 min before it was injected into the Parr reactor under a stream of argon. The schlenk tube was washed with MeOH (2 x 5 mL) and the washes injected into the reactor under a stream of argon. 1-octene (80.6 mmol), MeOH (8 mL) then anisole (internal standard, 0.5 mL) was injected into the Parr reactor before being pressurized with 50 bar CO and left to stir for 5 min before being sealed. The reactor was warmed to 100 °C then stirred for 2 h before being cooled to <10 °C in an ice-water bath. The Parr reactor was vented, and products were characterized by gas chromatography.

GC/MS data

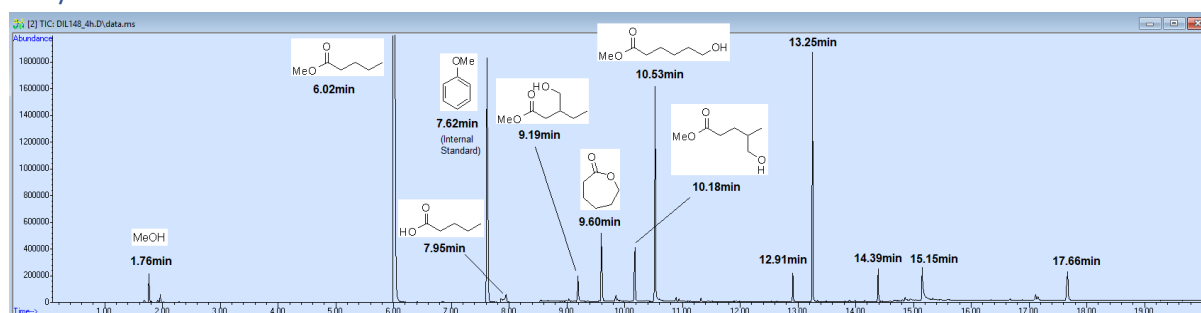


Figure S33. Gas chromatogram of the reaction mixture from Pd-catalysed hydroformylation of methyl 4-pentenoate (BCOPE, MSA/[Pd] = 40, Table S4/Table 5), diglyme solvent peak (8.00 – 8.50 min) removed for clarity.

Methyl 6-hydroxyhexanoate was not in the National Institute of Standards and Technology (NIST) mass spectrometry database, hence, the search did not show it as a match. However, methyl 6-hydroxyhexanoate and its branched isomer, methyl 5-hydroxy-4-methylpentanoate, were independently synthesized and analyzed to serve as reference standards.

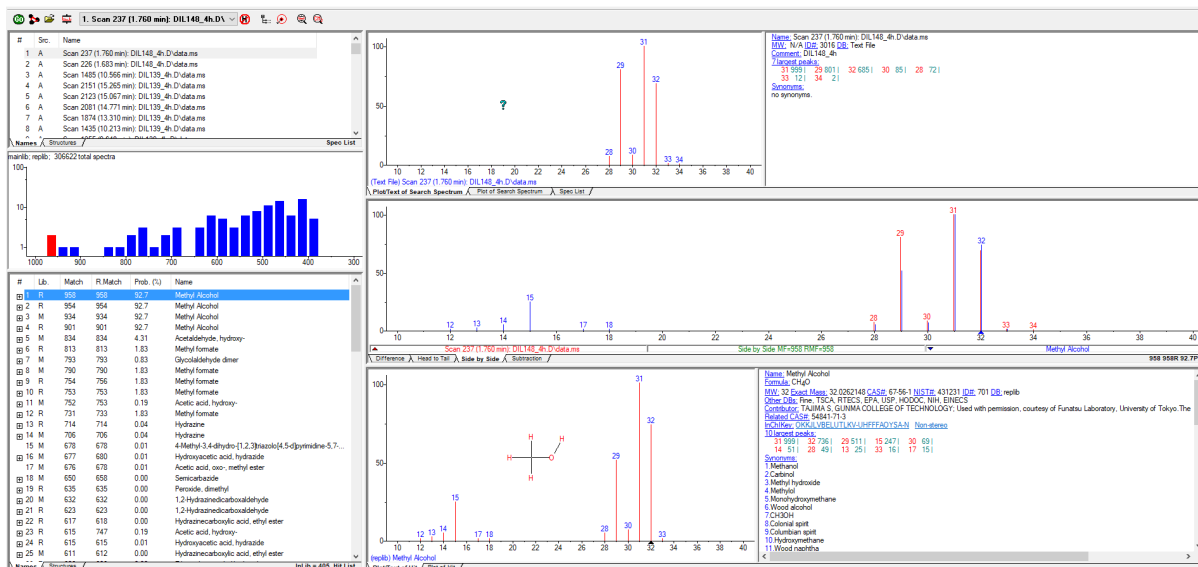


Figure S34. NIST mass spectrometry library search for peak at retention time = 1.76 min.

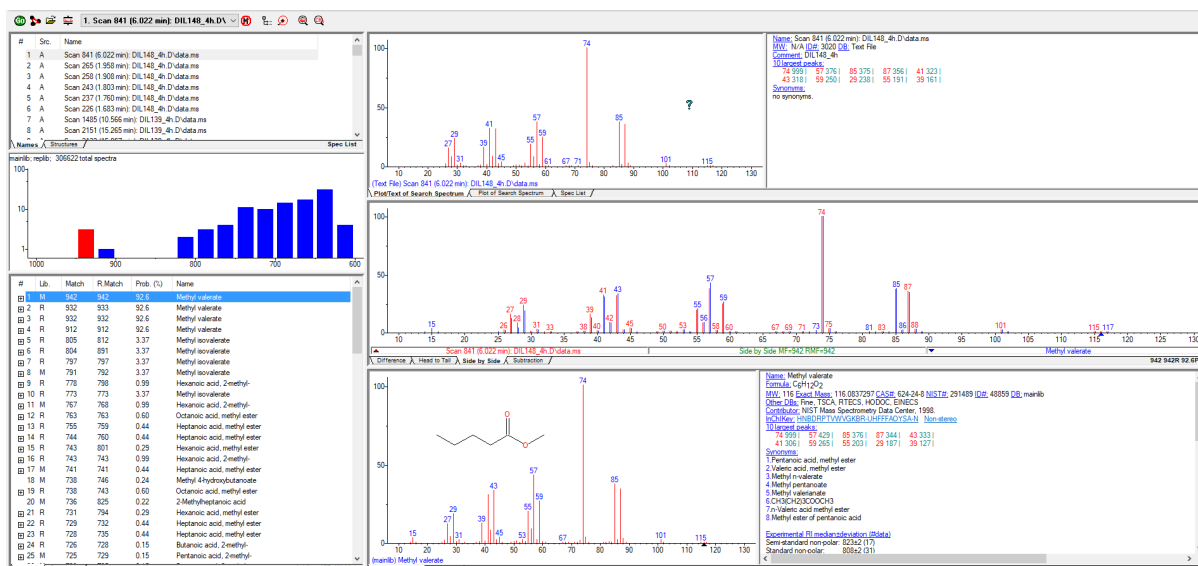


Figure S35. NIST mass spectrometry library search for peak at retention time = 6.02 min.

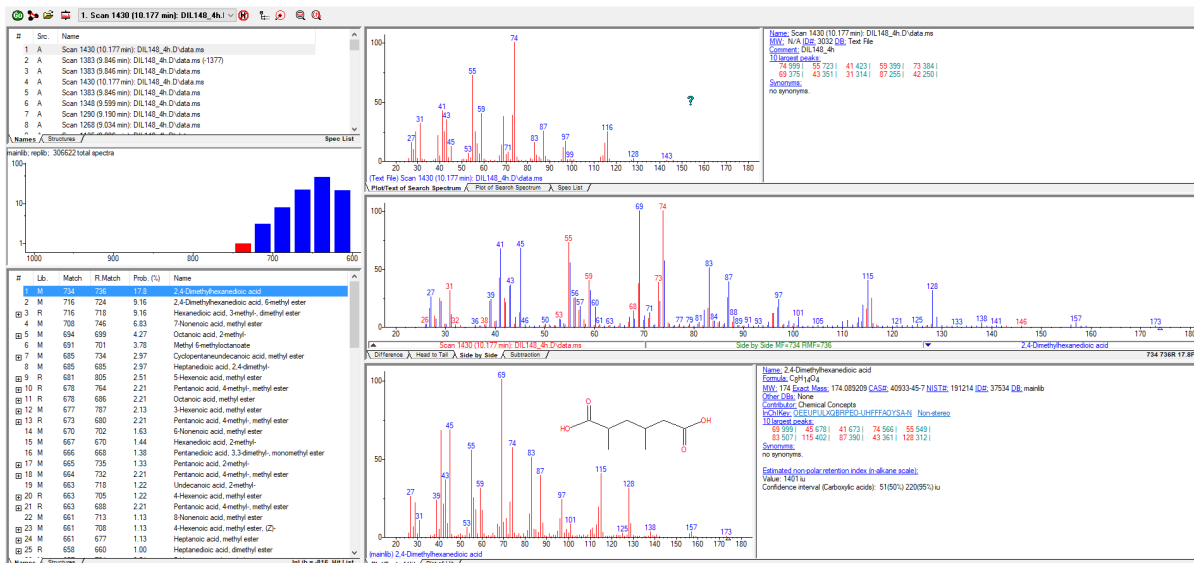


Figure S40. NIST mass spectrometry library search for peak at retention time = 10.18 min.

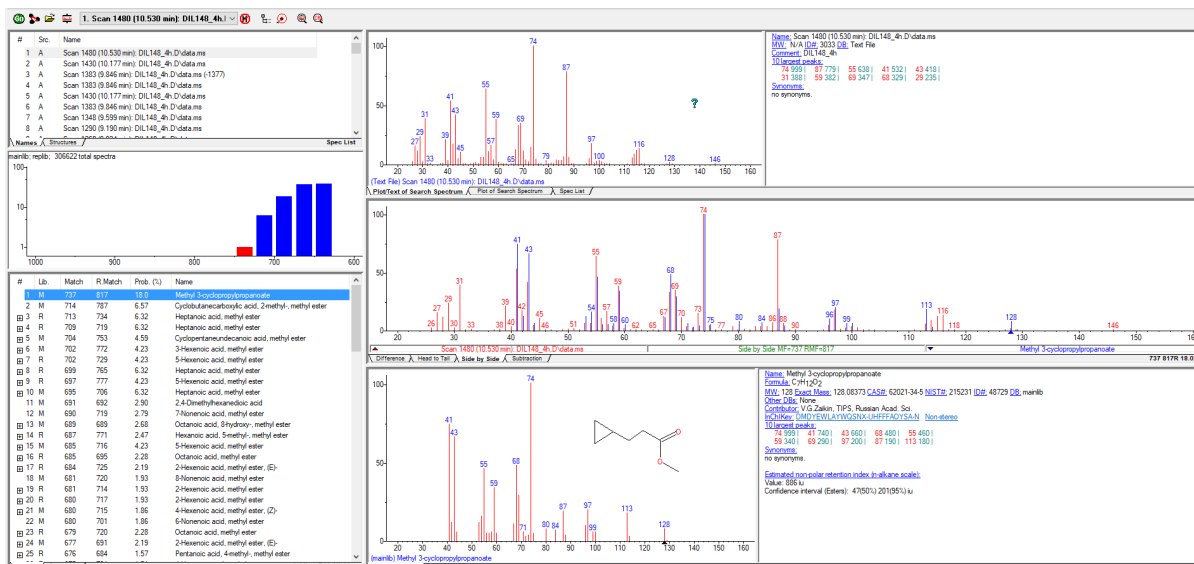


Figure S41. NIST mass spectrometry library search for peak at retention time = 10.53 min.

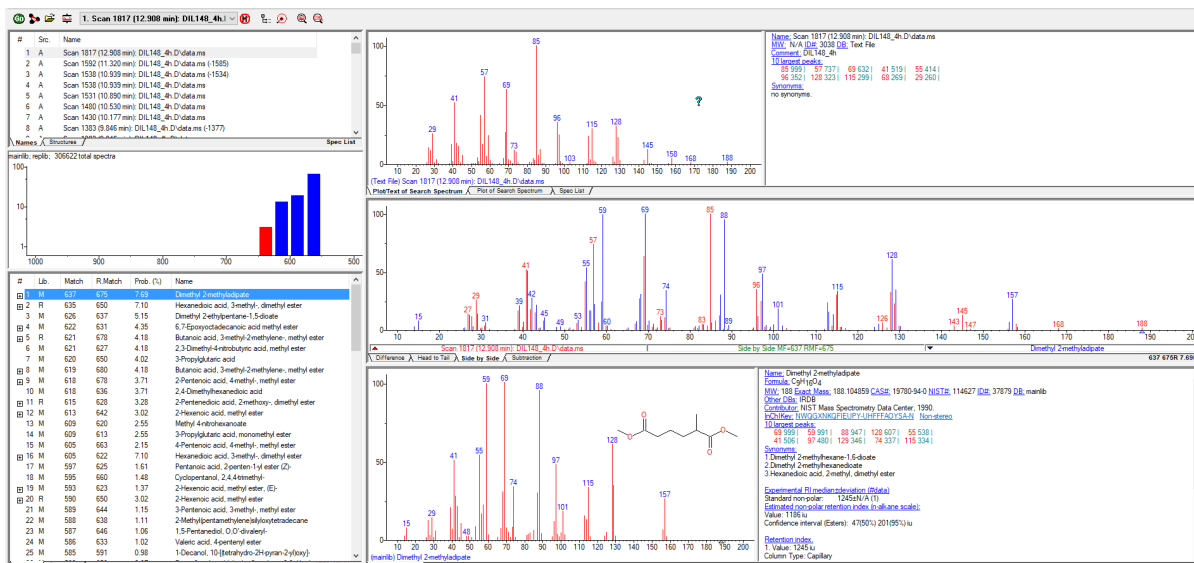


Figure S42. NIST mass spectrometry library search for peak at retention time = 12.91 min.

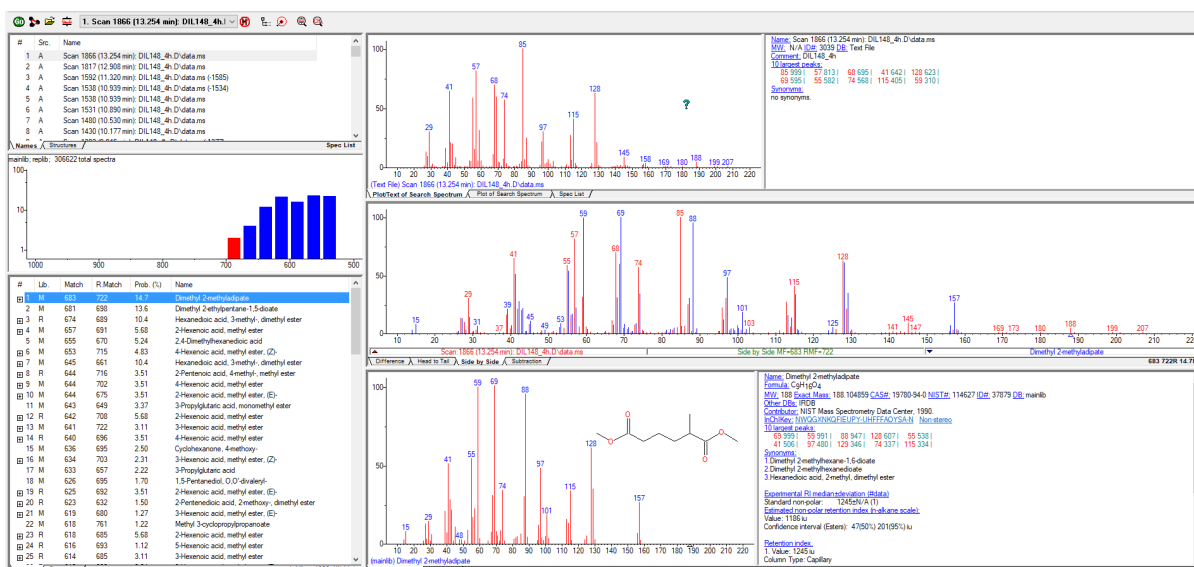


Figure S43. NIST mass spectrometry library search for peak at retention time = 13.25 min.

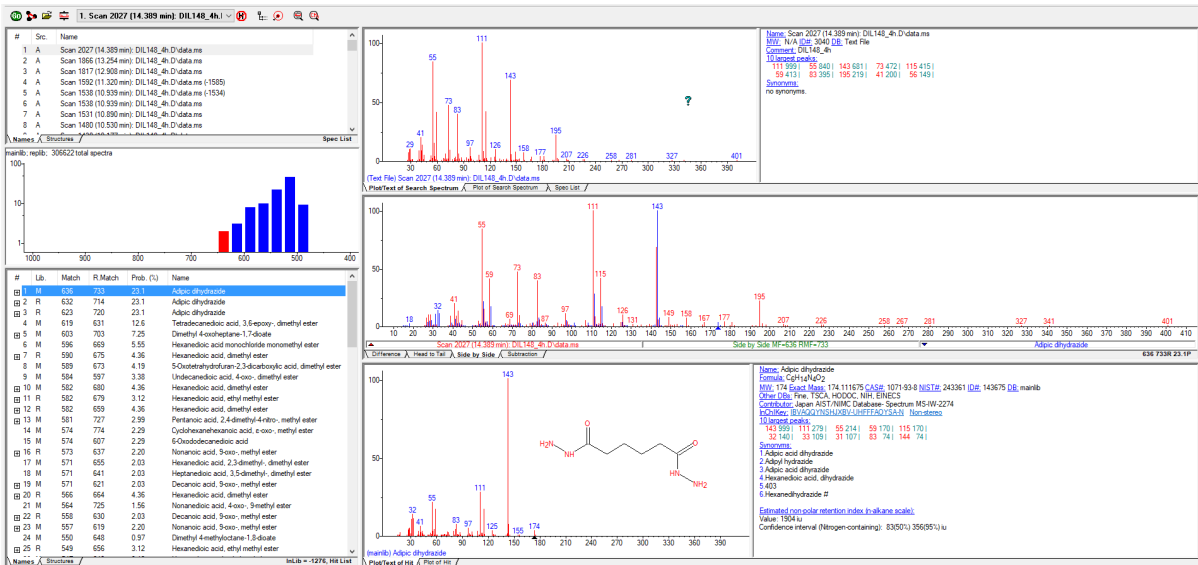


Figure S44. NIST mass spectrometry library search for peak at retention time = 14.39 min.

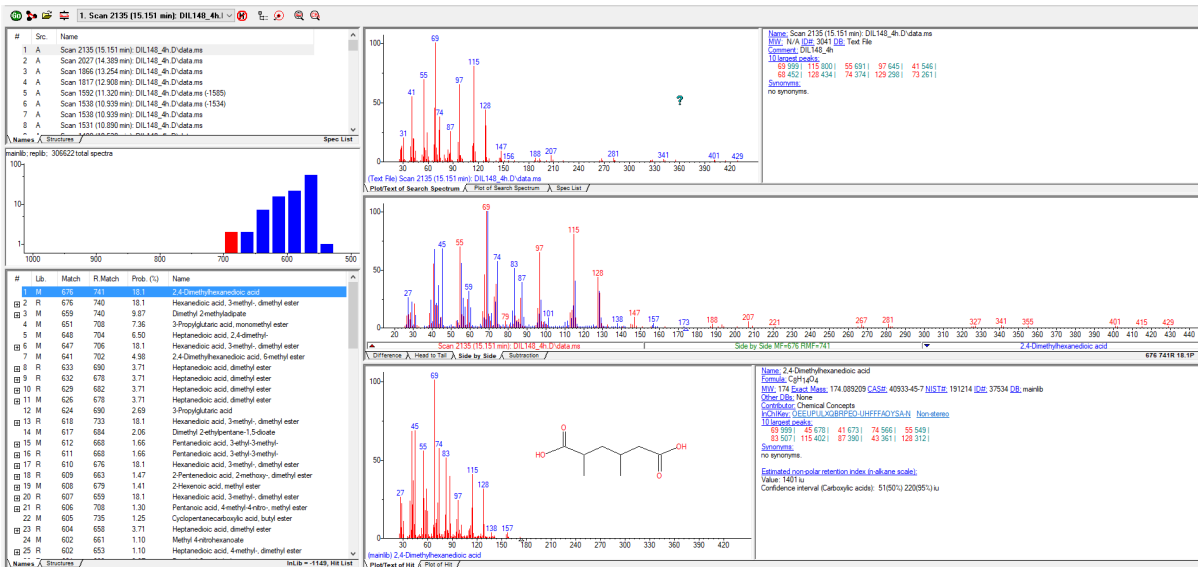


Figure S45. NIST mass spectrometry library search for peak at retention time = 15.15 min.

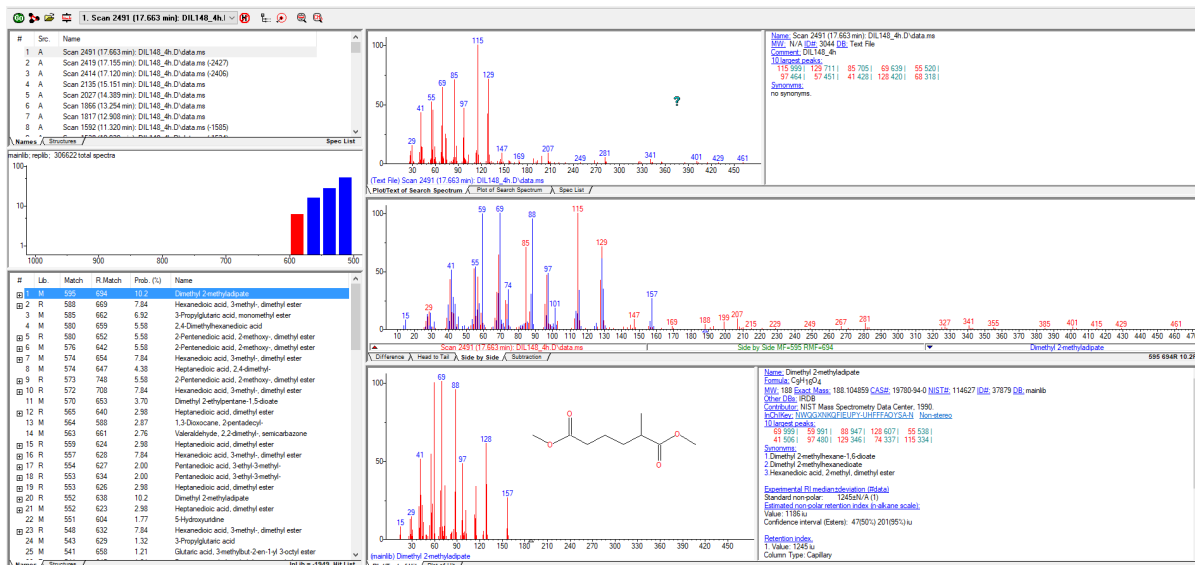


Figure S46. NIST mass spectrometry library search for peak at retention time = 17.66 min.

X-ray Diffraction (XRD)

The X-ray crystal structure of [Pd(BCOPE)Cl₂]

Crystal Data for [Pd(BCOPE)Cl₂]: C₁₈H₃₂Cl₂P₂Pd (M = 487.67 g/mol): monoclinic, space group P2₁/c (no. 14), $a = 11.7219(2)$ Å, $b = 12.3373(2)$ Å, $c = 13.6858(2)$ Å, $\beta = 96.2390(10)^\circ$, $V = 1967.47(5)$ Å³, $Z = 4$, $T = 295.79(10)$ K, $\mu(\text{CuK}\alpha) = 11.605$ mm⁻¹, $D_{\text{calc}} = 1.646$ g/cm³, 28422 reflections measured ($7.586^\circ \leq 2\theta \leq 145.426^\circ$), 3890 unique ($R_{\text{int}} = 0.0922$, $R_{\text{sigma}} = 0.0373$) which were used in all calculations. The final R_1 was 0.0535 ($I > 2\sigma(I)$) and wR_2 was 0.1522 (all data). CCDC 2042303.



Figure S47. The crystal structure of [Pd(BCOPE)Cl₂] (50% probability ellipsoids).

Table S5. Bond lengths [Å] for [Pd(BCOPE)Cl₂].

Atom	Atom	Length/Å
Pd1	P1	2.2840(15)
Pd1	P2	2.2752(15)
Pd1	Cl2	2.3673(15)
Pd1	Cl1	2.3686(17)
P1	C11	1.822(7)
P1	C15	1.829(7)
P1	C10	1.824(7)
P2	C1	1.833(7)
P2	C9	1.834(6)
P2	C5	1.828(7)
C11	C18	1.544(11)
C11	C12	1.534(9)
C1	C2	1.537(9)
C1	C8	1.535(9)
C9	C10	1.500(9)
C6	C5	1.531(10)
C6	C7	1.536(12)
C18	C17	1.535(12)
C14	C15	1.540(9)
C14	C13	1.531(9)
C15	C16	1.526(10)
C5	C4	1.554(10)
C3	C2	1.526(11)
C3	C4	1.531(10)

C13	C12	1.531(10)
C7	C8	1.532(12)
C17	C16	1.521(11)

Table S6. Bond angles [°] for [Pd(BCOPE)Cl₂].

Atom	Atom	Atom	Angle/°
P1	Pd1	Cl2	175.34(7)
P1	Pd1	Cl1	94.44(6)
P2	Pd1	P1	85.48(5)
P2	Pd1	Cl2	94.88(6)
P2	Pd1	Cl1	174.62(7)
Cl2	Pd1	Cl1	85.64(6)
C11	P1	Pd1	117.3(2)
C11	P1	C15	96.4(3)
C11	P1	C10	108.6(3)
C15	P1	Pd1	122.8(2)
C10	P1	Pd1	106.0(2)
C10	P1	C15	104.6(3)
C1	P2	Pd1	120.0(2)
C1	P2	C9	105.6(3)
C9	P2	Pd1	106.1(2)
C5	P2	Pd1	119.0(2)
C5	P2	C1	96.6(3)
C5	P2	C9	108.5(3)
C18	C11	P1	108.0(5)
C12	C11	P1	110.0(5)
C12	C11	C18	113.9(6)
C2	C1	P2	108.6(5)
C8	C1	P2	110.0(4)
C8	C1	C2	113.5(6)
C10	C9	P2	108.0(4)
C5	C6	C7	116.0(6)
C17	C18	C11	117.3(6)
C13	C14	C15	115.7(6)
C14	C15	P1	108.7(5)
C16	C15	P1	111.2(5)
C16	C15	C14	114.0(6)
C6	C5	P2	107.7(5)
C6	C5	C4	114.0(6)
C4	C5	P2	110.9(5)
C2	C3	C4	116.0(6)
C3	C2	C1	116.5(6)
C14	C13	C12	116.4(6)
C8	C7	C6	116.8(6)
C3	C4	C5	116.9(6)
C16	C17	C18	116.6(6)

C13 C12 C11 116.5(6)
 C7 C8 C1 117.3(6)
 C9 C10 P1 107.4(5)
 C17 C16 C15 116.3(6)

The X-ray crystal structure of [Pd(L2)Cl₂]

Crystal Data for [Pd(L2)Cl₂]: C₂₃H₃₄Cl₄P₂Pd (M=620.64 g/mol): monoclinic, space group P2₁/c (no. 14), *a* = 14.08010(10) Å, *b* = 13.60620(10) Å, *c* = 13.7056(2) Å, β = 106.2050(10)°, *V* = 2521.35(5) Å³, *Z* = 4, *T* = 296.7(3) K, μ(CuKα) = 11.107 mm⁻¹, *D*_{calc} = 1.635 g/cm³, 12231 reflections measured (9.222° ≤ 2θ ≤ 145.382°), 4858 unique (*R*_{int} = 0.0355, *R*_{sigma} = 0.0391) which were used in all calculations. The final *R*₁ was 0.0427 (*I* > 2σ(*I*)) and *wR*₂ was 0.1233 (all data). CCDC 2042304.

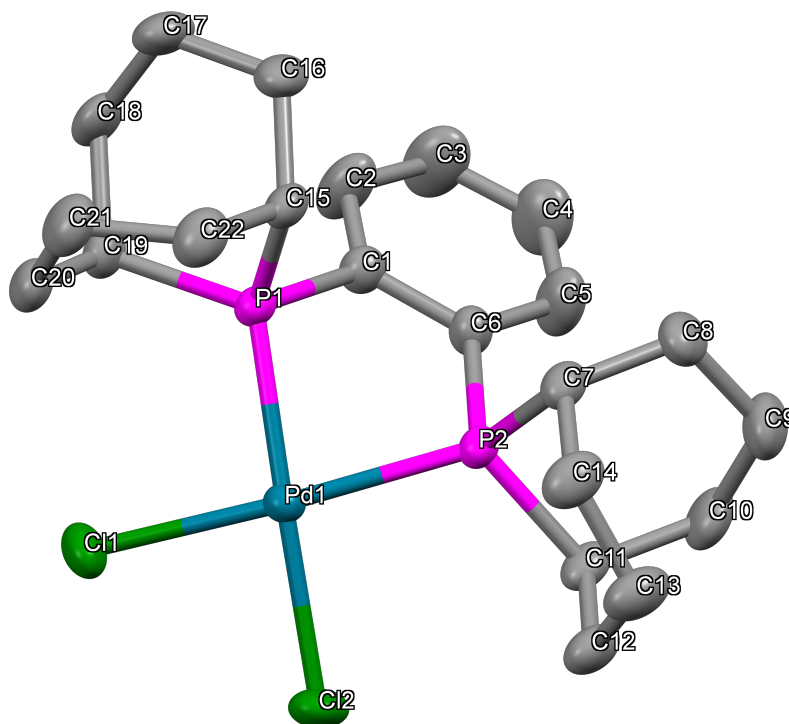


Figure S48. The crystal structure of [Pd(L₂)Cl₂] (50% probability ellipsoids).

Table S7. Bond lengths [Å] for [Pd(L₂)Cl₂].

Atom	Atom	Length/Å
Pd1	P1	2.2484(8)
Pd1	Cl1	2.3777(9)
Pd1	P2	2.2817(8)
Pd1	Cl2	2.3467(9)
P1	C1	1.823(4)
P1	C19	1.833(3)
P1	C15	1.834(4)
P2	C6	1.855(3)
P2	C7	1.835(3)
P2	C11	1.846(3)
C1	C6	1.405(5)
C1	C2	1.396(5)
C6	C5	1.391(5)
C19	C20	1.548(5)
C19	C18	1.546(5)
C15	C22	1.539(5)

C15	C16	1.543(5)
C7	C8	1.531(5)
C7	C14	1.538(5)
C11	C12	1.551(5)
C11	C10	1.540(5)
C20	C21	1.522(6)
C8	C9	1.540(6)
C22	C21	1.518(5)
C12	C13	1.514(5)
C16	C17	1.536(5)
C10	C9	1.533(6)
C14	C13	1.518(5)
C2	C3	1.391(6)
C4	C5	1.393(6)
C4	C3	1.356(7)
C18	C17	1.537(6)
C13	C23	1.743(6)
C23	C14	1.736(6)

Table S8. Bond angles [°] for [Pd(L2)Cl₂].

Atom	Atom	Atom	Angle/°
P1	Pd1	C11	94.02(3)
P1	Pd1	P2	82.31(3)
P1	Pd1	Cl2	173.97(4)
P2	Pd1	C11	165.85(3)
P2	Pd1	Cl2	96.46(3)
Cl2	Pd1	C11	85.76(3)
C1	P1	Pd1	99.93(11)
C1	P1	C19	115.32(16)
C1	P1	C15	106.24(16)
C19	P1	Pd1	117.85(12)
C19	P1	C15	95.95(15)
C15	P1	Pd1	122.00(11)
C6	P2	Pd1	99.59(11)
C7	P2	Pd1	125.91(12)
C7	P2	C6	107.19(16)
C7	P2	C11	95.52(15)
C11	P2	Pd1	115.74(12)
C11	P2	C6	113.28(16)
C6	C1	P1	115.2(2)
C2	C1	P1	125.6(3)
C2	C1	C6	119.3(3)
C1	C6	P2	115.5(2)
C5	C6	P2	125.7(3)
C5	C6	C1	118.8(3)
C20	C19	P1	106.4(2)
C18	C19	P1	113.3(3)
C18	C19	C20	112.0(3)
C22	C15	P1	107.9(3)
C22	C15	C16	115.8(3)
C16	C15	P1	109.3(3)
C8	C7	P2	109.3(3)
C8	C7	C14	114.5(3)
C14	C7	P2	108.8(3)
C12	C11	P2	107.3(2)

C10	C11	P2	113.2(3)
C10	C11	C12	112.0(3)
C21	C20	C19	116.2(3)
C7	C8	C9	118.2(3)
C21	C22	C15	116.6(3)
C13	C12	C11	115.9(3)
C17	C16	C15	117.1(3)
C9	C10	C11	116.9(3)
C13	C14	C7	115.9(3)
C3	C2	C1	120.6(4)
C3	C4	C5	120.3(4)
C22	C21	C20	113.5(3)
C10	C9	C8	118.5(3)
C12	C13	C14	113.9(3)
C17	C18	C19	117.6(3)
C6	C5	C4	120.8(4)
C16	C17	C18	117.3(3)
C4	C3	C2	120.1(4)
C14	C23	C13	112.0(3)

The X-ray crystal structure of [Pd(L6)Cl₂]

Crystal data for [Pd(L6)Cl₂]: C₂₂H₃₂Cl₂Pd₂, $M = 535.71$, monoclinic, P2₁/n (no. 14), $a = 7.62310(10)$ Å, $b = 19.9191(2)$ Å, $c = 14.50130(10)$ Å, $\beta = 94.9510(10)^\circ$, $V = 2193.74(4)$ Å³, $Z = 4$, $T = 295.3(3)$ K, $\mu(\text{CuK}\alpha) = 10.473$ mm⁻¹, $D_c = 1.622$ g cm⁻³, 21164 reflections measured ($7.56^\circ \leq 2\theta \leq 148.05^\circ$), F^2 refinement,¹⁻² 4389 unique ($R_{\text{int}} = 0.0508$, $R_{\text{sigma}} = 0.0338$) which were used in all calculations. The final R_1 was 0.0298 ($I > 2\sigma(I)$) and wR_2 was 0.0810 (all data). CCDC 2076315.

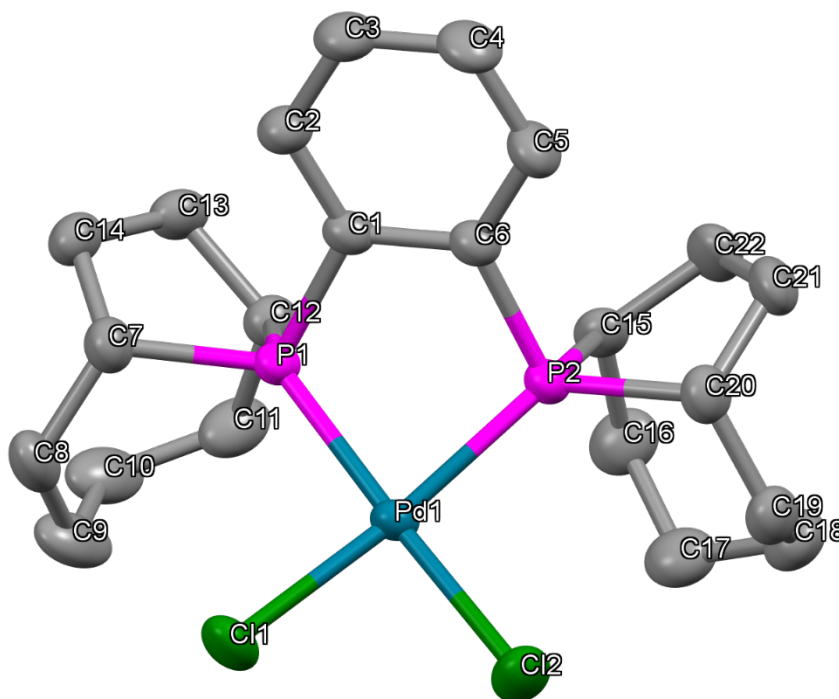


Figure S49. The crystal structure of [Pd(L6)Cl₂] (50% probability ellipsoids).

Table S9. Bond lengths [Å] and angles [°] for [Pd(L6)Cl₂].

Pd1	P2	2.2752(6)	C15	P2	C20	92.64(13)	
Pd1	P1	2.2661(6)	C20	P2	Pd1	125.20(9)	
Pd1	Cl2	2.3518(6)	C1	P1	Pd1	100.81(8)	
Pd1	Cl1	2.3383(7)	C1	P1	C12	105.22(12)	
P2	C6	1.831(3)	C1	P1	C7	106.57(13)	
P2	C15	1.841(3)	C12	P1	Pd1	122.41(9)	
P2	C20	1.857(3)	C12	P1	C7	92.74(13)	
P1	C1	1.833(2)	C7	P1	Pd1	127.12(10)	
P1	C12	1.840(3)	C6	C1	P1	115.91(19)	
P1	C7	1.853(3)	C2	C1	P1	124.0(2)	
C1	C6	1.402(4)	C2	C1	C6	120.1(2)	
C1	C2	1.390(4)	C13	C12	P1	102.20(19)	
C12	C13	1.536(4)	C11	C12	P1	113.7(2)	
C12	C11	1.535(4)	C11	C12	C13	113.8(2)	
C6	C5	1.391(3)	C1	C6	P2	115.19(18)	
C2	C3	1.381(4)	C5	C6	P2	126.0(2)	
C15	C16	1.535(4)	C5	C6	C1	118.8(2)	
C15	C22	1.546(4)	C3	C2	C1	120.4(3)	
C5	C4	1.390(4)	C16	C15	P2	112.27(19)	
C3	C4	1.378(5)	C16	C15	C22	115.7(3)	
C20	C19	1.546(4)	C22	C15	P2	103.5(2)	
C20	C21	1.534(4)	C4	C5	C6	120.6(3)	
C7	C14	1.556(4)	C4	C3	C2	120.0(3)	
C7	C8	1.533(4)	C19	C20	P2	114.47(19)	
C13	C14	1.537(5)	C21	C20	P2	103.80(19)	
C11	C10	1.515(5)	C21	C20	C19	109.5(2)	
C19	C18	1.533(5)	C14	C7	P1	104.0(2)	
C16	C17	1.520(4)	C8	C7	P1	114.2(2)	
C8	C9	1.526(6)	C8	C7	C14	111.4(2)	
C21	C22	1.543(5)	C12	C13	C14	110.4(2)	
C18	C17	1.511(5)	C3	C4	C5	120.2(3)	
C10	C9	1.531(6)	C13	C14	C7	111.7(2)	
			C10	C11	C12	117.5(3)	
P2	Pd1	Cl2	96.04(2)	C18	C19	C20	116.9(2)
P2	Pd1	Cl1	170.47(3)	C17	C16	C15	118.3(3)
P1	Pd1	P2	82.18(2)	C9	C8	C7	118.1(3)
P1	Pd1	Cl2	176.26(3)	C20	C21	C22	110.7(2)
P1	Pd1	Cl1	95.35(2)	C21	C22	C15	112.3(2)
Cl1	Pd1	Cl2	85.88(3)	C17	C18	C19	115.2(3)
C6	P2	Pd1	99.95(8)	C11	C10	C9	115.4(3)
C6	P2	C15	103.44(12)	C8	C9	C10	118.4(3)
C6	P2	C20	109.26(12)	C18	C17	C16	116.1(3)
C15	P2	Pd1	124.59(9)				

The X-ray crystal structure of [Pd₂(BCOPE)₂(μ-Cl)₂](O₃SCH₃)₂·(HO₃SCH₃)₂·(H₂O)

A suitable crystal of C₄₀H₈₀Cl₂O₁₃P₄Pd₂S₄ was selected and placed on a **SuperNova, Dual, Cu at zero, AtlasS2** diffractometer. The crystal was kept at 100.1(5) K during data collection. Using Olex2 [6], the structure was solved with the olex2.solve [7] structure solution program using Charge Flipping and refined with the ShelXL [8] refinement package using Least Squares minimisation.

Crystal Data for C₄₀H₈₀Cl₂O₁₃P₄Pd₂S₄ (*M* = 1304.86 g/mol): monoclinic, space group P2₁/c (no. 14), *a* = 12.15543(14) Å, *b* = 18.6842(2) Å, *c* = 23.4183(3) Å, β = 100.2268(11)°, *V* = 5234.14(11) Å³, *Z* = 4, *T* = 100.1(5) K, μ(MoKα) = 1.129 mm⁻¹, *D*_{calc} = 1.656 g/cm³, 135799 reflections measured (4.956° ≤ 2θ ≤ 58.402°), 12994 unique

($R_{\text{int}} = 0.0471$, $R_{\text{sigma}} = 0.0256$) which were used in all calculations. The final R_1 was 0.0311 ($I > 2\sigma(I)$) and wR_2 was 0.0656 (all data). CCDC 2076316.

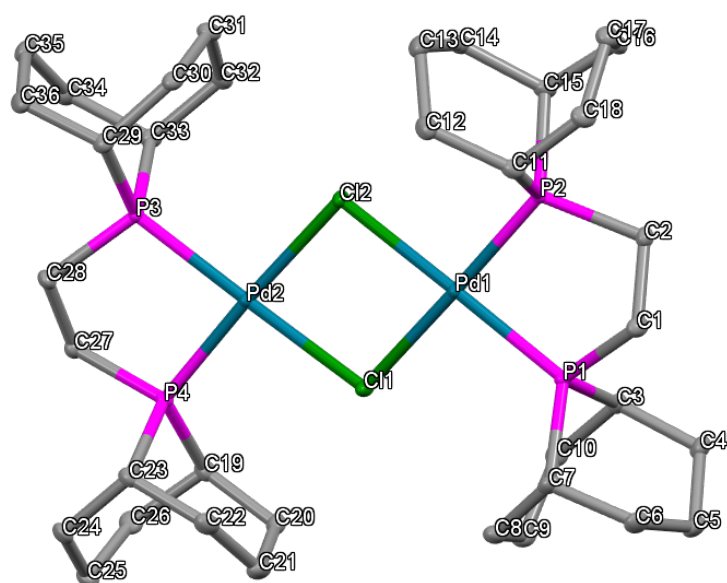


Figure S50. The crystal structure of the cation in $[\text{Pd}_2(\text{BCOPE})_2(\mu\text{-Cl})_2](\text{O}_3\text{SCH}_3)_2 \cdot (\text{HO}_3\text{SCH}_3)_2 \cdot (\text{H}_2\text{O})$ (50% probability ellipsoids).

Table S10. Bond Lengths for $[\text{Pd}_2(\text{BCOPE})_2(\mu\text{-Cl})_2](\text{O}_3\text{SCH}_3)_2 \cdot (\text{HO}_3\text{SCH}_3)_2 \cdot (\text{H}_2\text{O})$

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pd1	C12	2.4230(5)	S2	C38	1.754(3)
Pd1	C11	2.4027(5)	C6	C7	1.541(3)
Pd1	P4	2.2714(6)	C6	C5	1.541(3)
Pd1	P3	2.2744(6)	C27	C26	1.536(3)
Pd2	C12	2.4139(5)	C27	C28	1.541(4)
Pd2	C11	2.3969(5)	C10	C9	1.544(3)
Pd2	P1	2.2705(6)	C10	C11	1.536(3)
Pd2	P2	2.2629(6)	C9	C16	1.542(3)
P4	C34	1.820(2)	C12	C13	1.546(3)
P4	C22	1.828(2)	C12	C11	1.537(3)
P4	C17	1.829(2)	C16	C15	1.542(3)
P3	C33	1.822(2)	C7	C8	1.549(3)
P3	C31	1.831(2)	C20	C22	1.548(3)
P3	C25	1.827(2)	C20	C19	1.542(3)
P1	C7	1.828(2)	C30	C29	1.533(3)
P1	C35	1.823(2)	C30	C31	1.553(3)
P1	C1	1.831(2)	C13	C14	1.545(3)
S1	O3	1.4821(18)	C26	C25	1.541(3)
S1	O2	1.4471(19)	C36	C35	1.527(3)
S1	O1	1.4474(18)	C33	C34	1.525(3)
S1	C37	1.770(2)	C28	C31	1.547(3)
P2	C9	1.833(2)	C29	C32	1.534(3)
P2	C13	1.824(2)	C24	C17	1.548(3)
P2	C36	1.825(2)	C24	C23	1.540(3)
S4	O10	1.4761(19)	C3	C8	1.538(3)

S4	O11	1.4362(19)	C3	C2	1.538(3)
S4	O12	1.4597(18)	C32	C25	1.548(3)
S4	C40	1.759(3)	C21	C22	1.543(3)
S3	O8	1.4437(18)	C21	C23	1.537(3)
S3	O9	1.4382(19)	C15	C14	1.540(3)
S3	O7	1.5065(19)	C18	C19	1.537(3)
S3	C39	1.753(3)	C18	C17	1.539(3)
S2	O4	1.4355(19)	C2	C1	1.541(3)
S2	O5	1.5124(19)	C4	C5	1.541(3)
S2	O6	1.429(2)	C4	C1	1.548(3)

Table S11. Bond Angles for [Pd₂(BCOPE)₂(m-Cl)₂](O₃SCH₃)₂·(HO₃SCH₃)₂·(H₂O)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C11	Pd1	C12	80.637(18)	O4	S2	C38	107.44(15)
P4	Pd1	C12	97.954(19)	O5	S2	C38	104.22(14)
P4	Pd1	C11	178.29(2)	O6	S2	O4	116.66(12)
P4	Pd1	P3	84.94(2)	O6	S2	O5	108.07(13)
P3	Pd1	C12	177.07(2)	O6	S2	C38	109.21(16)
P3	Pd1	C11	96.48(2)	C5	C6	C7	116.38(19)
C11	Pd2	C12	80.940(18)	C26	C27	C28	117.85(19)
P1	Pd2	C12	176.92(2)	C11	C10	C9	115.52(19)
P1	Pd2	C11	97.12(2)	C10	C9	P2	107.77(15)
P2	Pd2	C12	97.584(19)	C16	C9	P2	110.97(15)
P2	Pd2	C11	178.19(2)	C16	C9	C10	113.11(19)
P2	Pd2	P1	84.31(2)	C11	C12	C13	116.58(19)
Pd2	C12	Pd1	98.623(19)	C9	C16	C15	117.22(19)
Pd2	C11	Pd1	99.67(2)	C6	C7	P1	110.55(15)
C34	P4	Pd1	107.54(8)	C6	C7	C8	113.77(19)
C34	P4	C22	109.70(11)	C8	C7	P1	107.82(15)
C34	P4	C17	106.65(11)	C19	C20	C22	117.04(19)
C22	P4	Pd1	114.02(8)	C29	C30	C31	115.4(2)
C22	P4	C17	97.69(11)	C12	C13	P2	109.37(16)
C17	P4	Pd1	120.61(8)	C14	C13	P2	106.85(15)
C33	P3	Pd1	108.01(7)	C14	C13	C12	116.02(19)
C33	P3	C31	107.00(11)	C27	C26	C25	116.6(2)
C33	P3	C25	109.42(11)	C35	C36	P2	106.32(15)
C31	P3	Pd1	120.60(7)	C34	C33	P3	107.75(15)
C25	P3	Pd1	113.47(7)	C27	C28	C31	117.34(19)
C25	P3	C31	97.66(11)	C30	C29	C32	115.30(19)
C7	P1	Pd2	122.68(8)	C23	C24	C17	116.40(19)
C7	P1	C1	97.40(10)	C30	C31	P3	107.27(15)
C35	P1	Pd2	107.91(8)	C28	C31	P3	110.73(16)
C35	P1	C7	107.90(11)	C28	C31	C30	113.46(19)
C35	P1	C1	107.69(11)	C8	C3	C2	115.71(19)
C1	P1	Pd2	112.19(7)	C29	C32	C25	116.72(19)
O3	S1	C37	105.51(12)	C36	C35	P1	106.87(15)
O2	S1	O3	111.60(11)	C23	C21	C22	116.32(19)
O2	S1	O1	114.20(12)	C10	C11	C12	116.45(19)
O2	S1	C37	107.39(12)	C14	C15	C16	116.95(19)
O1	S1	O3	110.57(11)	C15	C14	C13	116.14(19)
O1	S1	C37	107.03(12)	C33	C34	P4	108.66(15)
C9	P2	Pd2	120.63(7)	C3	C8	C7	116.98(19)
C13	P2	Pd2	114.49(7)	C20	C22	P4	107.54(15)

C13	P2	C9	97.67(10)	C21	C22	P4	109.77(16)
C13	P2	C36	107.70(11)	C21	C22	C20	114.36(18)
C36	P2	Pd2	107.68(7)	C19	C18	C17	116.99(19)
C36	P2	C9	107.78(11)	C3	C2	C1	116.19(19)
O10	S4	C40	105.62(13)	C18	C19	C20	117.40(18)
O11	S4	O10	111.81(11)	C5	C4	C1	117.34(19)
O11	S4	O12	114.78(12)	C6	C5	C4	116.81(19)
O11	S4	C40	108.29(13)	C24	C17	P4	107.76(15)
O12	S4	O10	110.92(11)	C18	C17	P4	110.38(15)
O12	S4	C40	104.72(12)	C18	C17	C24	113.49(18)
O8	S3	O7	110.36(11)	C21	C23	C24	115.13(19)
O8	S3	C39	107.25(13)	C26	C25	P3	107.72(15)
O9	S3	O8	116.45(11)	C26	C25	C32	114.51(19)
O9	S3	O7	109.08(11)	C32	C25	P3	109.54(16)
O9	S3	C39	108.67(12)	C2	C1	P1	109.97(16)
O7	S3	C39	104.30(13)	C2	C1	C4	114.51(19)
O4	S2	O5	110.52(11)	C4	C1	P1	107.54(15)

Table S12. Hydrogen Bonds for [Pd₂(BCOPE)₂(m-Cl)₂](O₃SCH₃)₂·(HO₃SCH₃)₂·(H₂O)

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O13	H13A	O3	0.98(4)	1.51(4)	2.483(3)	171(4)
O13	H13B	O10 ¹	0.98(4)	1.52(4)	2.498(3)	174(3)
O13	H13C	O12 ²	0.80(4)	1.77(4)	2.564(3)	166(4)
O5	H7A	O7	1.02(6)	1.42(6)	2.430(3)	171(5)

¹-X,-Y,1-Z; ²1+X,+Y,+Z

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