Supporting Information

Direct Observation of C−H Cyclopalladation at Tertiary Positions Enabled by an *Exo*-Directing Group

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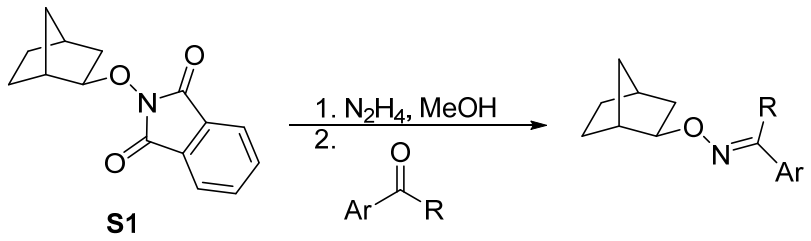
I. General Considerations

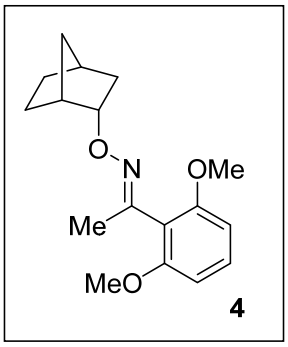
Unless otherwise noted, all experiments were carried out under air atmosphere. The other reagents and solvents were directly used from the supplier without further purification unless noted. Analytical thin-layer chromatography (TLC) was carried out using 0.2 mm commercial silica gel plates (silica gel 60, F254, EMD chemical). The vials (1 dram, 15×45 mm with PTFE lined cap attached) were purchased from Qorpak and dried in an oven overnight and cooled in air. Infrared spectra were recorded on a Nicolet iS5 FT-IR Spectrometer using neat thin film technique. High-resolution mass spectra (HRMS) were obtained on a Karatos MS9 and are reported as m/z (relative intensity). Accurate masses are reported for the molecular ion $[M+Na]^+$, $[M+H]^+$ or $[2M-Cl]^+$. Nuclear magnetic resonance spectra (^1H NMR and ^{13}C NMR) were recorded with Varian Gemini (400 MHz, ^1H at 400 MHz, ^{13}C at 100 MHz) or Varian Gemini (500 MHz, ^1H at 500 MHz, ^{13}C at 125 MHz). For $CDCl_3$ solutions the chemical shifts are reported as parts per million (ppm) referenced to residual protium or carbon of the solvents; $CHCl_3$ δ H (7.26 ppm) and $CDCl_3$ δ C (77.16 ppm). Coupling constants are reported in Hertz (Hz). Data for ^1H NMR spectra are reported as follows: chemical shift (ppm, referenced to protium; s = singlet, d = doublet, t = triplet, q = quartet, p = pentet (quintet), dd = doublet of doublets, td = triplet of doublets, ddd = doublet of doublet of doublets, m = multiplet, coupling constant (Hz), and integration).

II. Preparation and Characterization of Oxime Starting Materials



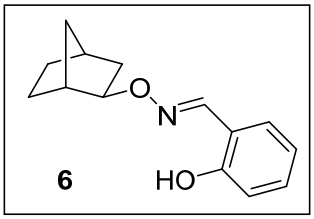
S1

General Procedure: To a solution of compound **S1** (1 equiv) in MeOH (1.5 mL/mmol) was added hydrazine hydrate (1 equiv) at room temperature. After 1.5 h, the corresponding aldehyde or ketone was added (when ketone was used, 2 drops of AcOH were added). After the reaction was complete (30 mins for aldehyde and overnight for ketone), the solvent was removed under *vacuo*. The desired oxime product was further purified by flash column chromatography on silica gel. Compounds **S1** and **1a** were prepared according to our previous reported procedure.[1]



4

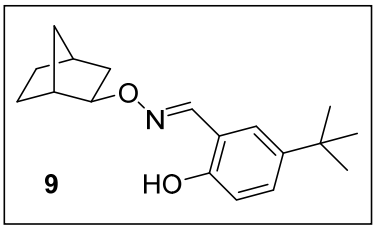
Compound 4: The reaction was conducted on a 1.5 mmol scale with 2,6-dimethoxyacetophenone. The title compound was isolated as a white solid (0.4023 g, 93%). **R_f value**= 0.1 in Hexanes/EA= 10:1. **Melting Point** (air): 87-89 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 (t, *J* = 8.4 Hz, 1H), 6.55 (d, *J* = 8.4 Hz, 2H), 4.29 (ddt, *J* = 7.2, 2.3, 1.0 Hz, 1H), 3.79 (s, 6H), 2.50 – 2.44 (m, 1H), 2.27 (td, *J* = 4.1, 1.7 Hz, 1H), 2.07 (s, 3H), 1.67 – 1.41 (m, 5H), 1.15 – 1.03 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.33, 152.37, 129.72, 116.36, 104.27, 85.31, 56.11, 41.21, 38.30, 35.53, 34.89, 28.80, 24.29, 16.64. **FT-IR** (neat): 2955, 2870, 2836, 1709, 1595, 1471, 1432, 1351, 1304, 1250 cm^{-1}. **HRMS** (ESI) Calcd. For $C_{17}H_{23}NO_3Na^+$ $[M+Na]^+$: 312.1570, Found: 312.1579.



6

Compound 6: The reaction was conducted on a 1.0 mmol scale with salicylaldehyde. The title compound was isolated as a colorless oil (0.2119 g, 92%). **R_f value**= 0.6 in Hexanes/EA= 10:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.08 (d, *J* = 0.4 Hz, 1H), 8.14 (s, 1H), 7.29 – 7.24 (m, 1H), 7.14

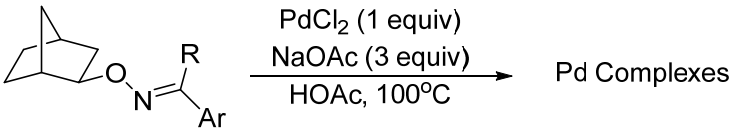
(ddt, *J* = 7.7, 1.7, 0.5 Hz, 1H), 6.98 (ddt, *J* = 8.3, 1.1, 0.5 Hz, 1H), 6.93 – 6.87 (m, 1H), 4.25 (ddt, *J* = 7.1, 2.3, 1.0 Hz, 1H), 2.53 – 2.47 (m, 1H), 2.34 – 2.28 (m, 1H), 1.72 – 1.65 (m, 1H), 1.60 – 1.45 (m, 4H), 1.18 – 1.06 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.56, 151.29, 131.05, 130.67, 119.63, 116.78, 116.77, 86.81, 40.87, 37.96, 35.45, 34.71, 28.60, 24.23. **FT-IR** (neat): 3188, 2960, 2872, 1622, 1609, 1494, 1394, 1354, 1264 cm^{-1}.**HRMS** (ESI) Calcd. For $C_{14}H_{17}NO_2^+$ $[M+H]^+$: 232.1332, Found: 232.1331.



9

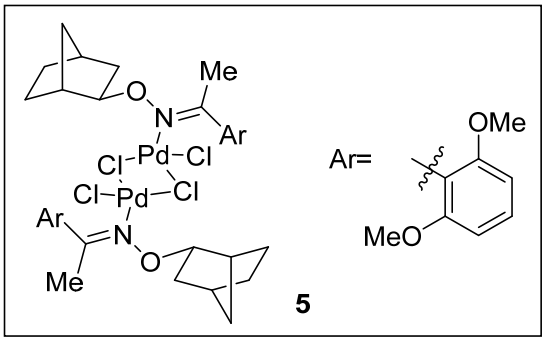
Compound 9: The reaction was conducted on a 10.0 mmol scale with 5-(*tert*-butyl)-2-hydroxybenzaldehyde. The title compound was isolated as a yellow oil (2.4041 g, 84%). **R_f value**= 0.5 in Hexanes/EA= 10:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.90 (s, 1H), 8.14 (s, 1H), 7.30 (dd, *J* = 8.6, 2.5 Hz, 1H), 7.11 (d, *J* = 2.5 Hz, 1H), 6.94 – 6.89 (m, 1H), 4.24 (ddt, *J* = 7.1, 2.2, 1.0 Hz, 1H), 2.49 (d, *J* = 4.9 Hz, 1H), 2.34 – 2.26 (m, 1H), 1.67 (ddd, *J* = 13.4, 7.1, 2.5 Hz, 1H), 1.56 – 1.41 (m, 4H), 1.29 (s, 9H), 1.12 (dddd, *J* = 11.5, 6.8, 3.8, 2.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.29, 151.75, 142.32, 128.32, 127.23, 116.31, 116.04, 86.69, 40.86, 37.97, 35.46, 34.69, 34.09, 31.55, 28.63, 24.24. **FT-IR** (neat): 3188, 2960, 2872, 1622, 1609, 1494, 1394, 1354, 1264 cm^{-1}. **HRMS** (ESI) Calcd. For $C_{18}H_{25}NO_2Na^+$ $[M+Na]^+$: 310.1778, Found: 310.1785.

III. Preparation Procedure for the Palladium Complexes



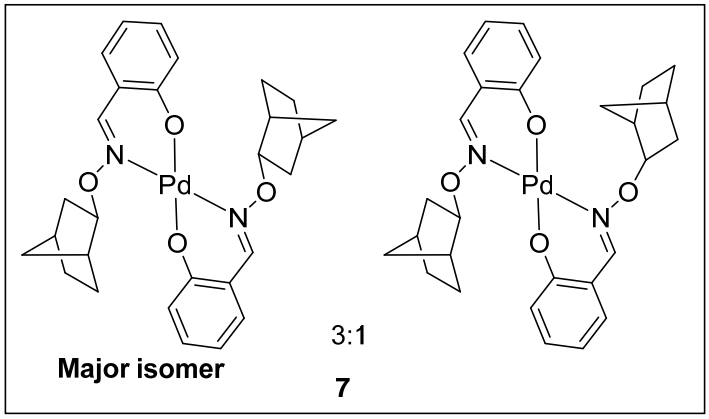
General Procedure: $PdCl_2$ (17.7 mg, 0.1 mmol, 1 equiv), NaOAc (24.6mg, 0.3 mmol, 3 equiv) and the oxime substrate (0.1 mmol, 1 equiv) were added in a Schlenk flask, followed by 0.5 mL

AcOH. The flask was freeze-pump-thawed for three times and charged with Ar, and then the reaction was stirred at 100 °C. The reaction was monitored by TLC and generally finished within 2. The mixture was purified according to the specific procedure in each case. In general the crystal structures are obtained by slow evaporation of DCM and hexanes, unless otherwise mentioned.



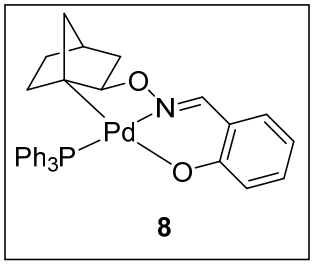
5

Pd complex **5**: The reaction was conducted on a 0.1 mmol scale. After the reaction was complete in 2h, the reaction was diluted with DCM and sequentially washed with water, and brine. The crude mixture was purified by column chromatography to give the title complex as a yellow solid (0.0319 g, 68%). However, the complex could form a number of isomers in solution and the NMR spectra (-50 °C) are difficult to understand. **R_f value**= 0.27 in Hexanes/EA= 3:1. **Melting Point** (air): decompose at 120 °C. **FT-IR** (neat): 2959, 2872, 2837, 1623, 1596, 1474, 1431, 1356, 1306, 1291, 1257 cm^{-1}. **HRMS** (ESI) Calcd. For $C_{34}H_{36}Cl_3N_4O_2Pd_2^+$ $[2M\text{-}Cl]^+$: 850.9970, Found: 850.9978.



7

Pd complex **7**: The reaction was conducted on a 0.1 mmol scale. After the reaction was finished in 1h, the reaction was diluted with DCM and sequentially washed with water, and brine. The crude mixture was purified by column chromatography to give the title compound as a yellow-orange solid (0.0137 g, 97%). The mixture contains an inseparable diastereomers in 3:1 ratio, which is determined by NMR. Both of the diastereomers are **not** C2-symmetrical according to the X-ray structure presumably due to the steric hinderance of norbornyl skeleton. **R_f value**= 0.4 in Hexanes/EA= 5:1. **Melting Point** (air): decompose at 205 ^{o}C. **^{1}H NMR** for the distinctive peaks of major isomer (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.29 (ddd, *J* = 8.7, 4.5, 2.6 Hz, 1H), 7.14 (ddd, *J* = 7.9, 3.1, 1.8 Hz, 1H), 6.91 (d, *J* = 8.5 Hz, 1H), 6.61 (dddd, *J* = 7.9, 6.8, 2.0, 1.1 Hz, 1H), 4.58 (ddt, *J* = 15.0, 7.4, 2.1 Hz, 1H), 2.40 (dd, *J* = 23.7, 4.9 Hz, 1H), 2.34 (s, 1H), 1.76 (ddt, *J* = 13.7, 7.3, 2.3 Hz, 1H), 1.64 (dd, *J* = 5.4, 2.7 Hz, 2H), 1.56 – 1.41 (m, 3H), 1.13 – 1.03 (m, 2H). **^{13}C NMR** for the distinctive peaks of major isomer (125 MHz, $CDCl_3$) δ 164.56, 164.54, 157.52, 135.10, 133.41, 120.41, 120.37, 115.49, 115.46, 114.63, 114.55, 88.25, 88.19, 39.05, 38.79, 37.63, 37.55, 35.52, 35.50, 35.00, 34.83, 28.43, 28.42, 24.09, 23.95. **FT-IR** (neat): 2958, 2870, 1602, 1533, 1465, 1440, 1350, 1307, 1194, 1149, 1128, 1070, 1031 cm^{-1}. **HRMS** (ESI) Calcd. For $C_{26}H_{36}ClN_2O_6Pd_2^+$ $[M]^+$: 721.0337, Found: 721.0331.

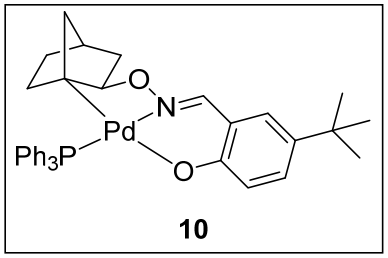


8

Pd complex **8**: The reaction was conducted on a 0.5 mmol scale. After the reaction was finished in 1h, 1 equiv of PPh_3 was added and the reaction was stirred for another 30 mins. The solid was suspended with a large amount of DCM and washed with hexanes and water three times. After addition of hexanes to the solution, a yellow solid was precipitated and collected to give Pd complex **8** as a yellow solid (0.1435 g, 96%). The crystal was obtained by dissolving the complex in a large amount of DCM, followed by slow diffusion with hexanes.

Complex **8** has very low solubility in most organic solvents. For example, its saturated concentration in deuterated DCM was too low to obtain any useful NMR spectra even after a large number of scans. More polar NMR solvents, such as d_6-DMSO, unfortunately did not significantly improve the solubility. On the other hand, the use of other nitrogen ligands, such as pyridine and MeCN, didn't provide the desired cyclopalladation complex. In addition, use of $P(n\text{-}Bu)_3$ also failed to provide the desired product, suggesting the electronic properties of the incoming ligand is also important for the cyclopalladation step.

Melting Point (air): decompose at 200 ^{o}C. **FT-IR** (neat): 2955, 2870, 2836, 1709, 1595, 1471, 1432, 1351, 1304, 1250 cm^{-1}. **HRMS** (ESI) Calcd. For $C_{32}H_{30}NO_2PPd^{+}$ $[M+H]^{+}$: 598.1134, Found: 598.1128.

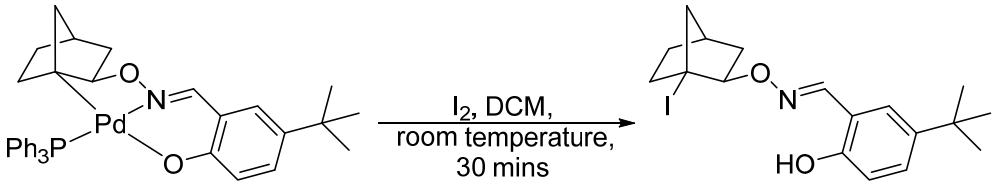


10

Pd complex **10**: The reaction was conducted on a 0.1 mmol scale. After the reaction was finished in 2h, 1 equiv of PPh_3 was added and the reaction was purified by column chromatography to give the title complex as a yellow solid (0.0269 g, 82%). **R_f value**= 0.4 in Hexanes/EA= 3:1. **Melting Point** (air): decompose at 215 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.3 Hz, 1H), 7.77 (ddd, *J* = 11.1, 8.0, 1.6 Hz, 6H), 7.55 – 7.32 (m, 9H), 7.21 (dd, *J* = 8.9, 2.7 Hz, 1H), 6.99 (d, *J* = 2.7 Hz, 1H), 6.49 (d, *J* = 8.9 Hz, 1H), 4.05 (dt, *J* = 6.3, 1.6 Hz, 1H), 1.90 (t, *J* = 4.3 Hz, 1H), 1.56 (ddt, *J* = 13.0, 4.3, 2.5 Hz, 1H), 1.44 – 1.39 (m, 1H), 1.37 – 1.32 (m, 1H), 1.25 (s, 9H), 1.03 – 0.91 (m, 2H), 0.81 (ddd, *J* = 11.2, 6.8, 4.1 Hz, 1H), 0.67 – 0.56 (m, 1H), 0.21 (dq, *J* = 9.7, 1.3 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.31, 148.62 (d, $^{4}J_{p,c}$ = 2.8 Hz), 135.43, 135.22 (d, $^{3}J_{p,c}$ = 12.3 Hz), 131.21, 130.48 (d, $^{3}J_{p,c}$ = 46.1 Hz), 130.44 (d, $^{4}J_{p,c}$ = 2.4 Hz), 128.80, 128.06 (d, $^{4}J_{p,c}$ = 10.5 Hz), 122.30, 115.24, 92.43, 60.93 (d, $^{2}J_{p,c}$ = 5.0 Hz), 39.03, 35.11, 34.21, 33.62, 32.46 (d, $^{3}J_{p,c}$ = 6.1 Hz), 31.56, 29.64 (d, $^{3}J_{p,c}$ = 3.5 Hz). **^{31}P NMR** (160 MHz, $CDCl_3$) δ

34.93. **FT-IR** (neat): 3054, 2952, 2860, 1612, 1518, 1469, 1435 cm^{-1}. **HRMS** (ESI) Calcd. For $C_{36}H_{38}NO_2PPd^+$ $[M+H]^+$: 654.1761, Found: 654.1776.

IV. Reaction of Pd Complex 10 with Iodine

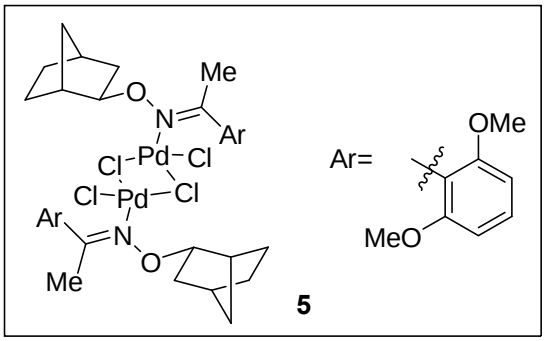


10 **11**, 54%

In a vial charged with Pd complex **10** (0.0654 g, 0.1 mmol, 1 equiv) and I_2 (0.0284g, 0.1 mmol, 1 equiv), 1 mL of DCM was added as solvent. The reaction was stirred at room temperature for 30 min. After the reaction was finished, the reaction was purified by column chromatography to give the title compound as a dark oil light sensitive (0.0222 g, 54%). **R_f value**= 0.3 in Hexanes/EA= 10:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.65 (s, 1H), 8.25 (s, 1H), 7.31 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.13 (d, *J* = 2.4 Hz, 1H), 6.92 (dd, *J* = 8.6, 0.5 Hz, 1H), 4.21 (td, *J* = 4.9, 1.4 Hz, 1H), 2.24 – 2.17 (m, 1H), 2.14 – 2.04 (m, 2H), 1.87 – 1.78 (m, 3H), 1.74 – 1.53 (m, 3H), 1.29 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.22, 152.38, 142.42, 128.61, 127.49, 116.38, 115.89, 87.91, 47.05, 40.39, 39.45, 39.22, 34.81, 34.11, 31.55, 31.43. **FT-IR** (neat): 3217, 2961, 2871, 1621, 1608, 1580, 1494, 1462, 1439, 1384, 1364, 1262 cm^{-1}. **HRMS** (ESI) Calcd. For $C_{18}H_{24}INO_2^+$ $[M+H]^+$: 414.0924, Found: 414.0924.

V. X-ray Structures

X-ray structure data of Pd complex **5**:



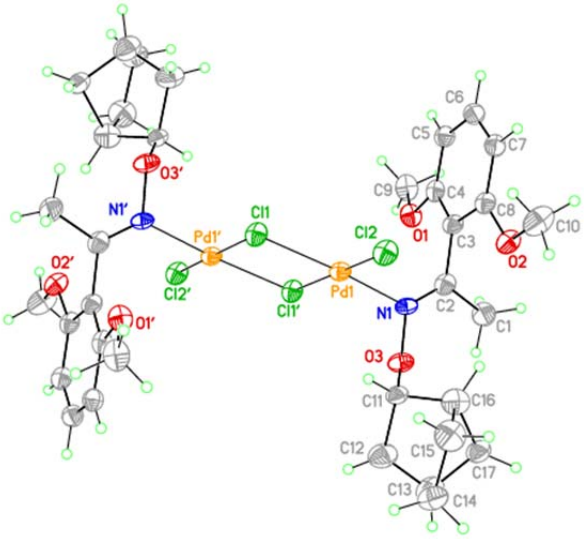


Figure S1. ORTEP structure of Pd complex **5** (displacement ellipsoids are scaled to the 50% probability level; all solvent molecules omitted for clarity).

Table S1.1. Crystal data and structure refinement for Pd complex **5**.

Empirical formula	C34 H46 Cl4 N2 O6 Pd2	
Formula weight	933.33	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 14.9412(8) Å	α= 90°.
	b = 8.7902(6) Å	β= 116.895(6)°.
	c = 15.9120(9) Å	γ = 90°.

Volume	1863.8(2) $Å^3$
Z	2
Density (calculated)	1.663 Mg/m^3
Absorption coefficient	10.797 mm^{-1}
F(000)	944
Crystal size	0.076 x 0.051 x 0.025 mm^3
Theta range for data collection	3.370 to 74.553°.
Index ranges	-18<=h<=18, -10<=k<=7, -19<=l<=19
Reflections collected	8709
Independent reflections	3662 [R(int) = 0.0431]
Completeness to theta = 67.684°	99.5 %
Absorption correction	Gaussian
Max. and min. transmission	0.940 and 0.872
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3662 / 0 / 220
Goodness-of-fit on F^2	1.051
Final R indices [I>2sigma(I)]	R1 = 0.0498, wR2 = 0.1102
R indices (all data)	R1 = 0.0687, wR2 = 0.1201
Extinction coefficient	n/a
Largest diff. peak and hole	0.727 and -0.782 $e.Å^{-3}$

Table S1.2. Bond lengths [Å] and angles [°] for Pd complex **5**.

C1-C2	1.507(8)	C11-C16	1.522(10)
C1-H1A	0.98	C11-C12	1.552(9)
C1-H1B	0.98	C11-H11	1.00
C1-H1C	0.98	C12-C13	1.434(11)
C2-N1	1.268(8)	C12-H12A	0.99
C2-C3	1.500(8)	C12-H12B	0.99
C3-C8	1.390(8)	C13-C17	1.505(11)
C3-C4	1.394(9)	C13-C14	1.530(10)
C4-O1	1.361(7)	C13-H13	1.00
C4-C5	1.389(9)	C14-C15	1.539(11)
C5-C6	1.383(8)	C14-H14A	0.99
C5-H5	0.9500	C14-H14B	0.99
C6-C7	1.362(9)	C15-C16	1.497(11)
C6-H6	0.9500	C15-H15A	0.99
C7-C8	1.397(8)	C15-H15B	0.99
C7-H7	0.9500	C16-C17	1.614(9)
C8-O2	1.357(7)	C16-H16	1.00
C9-O1	1.430(8)	C17-H17A	0.99
C9-H9A	0.98	C17-H17B	0.99
C9-H9B	0.98	N1-O3	1.408(6)
C9-H9C	0.98	N1-Pd1	2.012(5)
C10-O2	1.439(7)	Cl1-Pd1	2.3223(14)
C10-H10A	0.98	Cl1-Pd1#1	2.3408(15)
C10-H10B	0.98	Cl2-Pd1	2.2698(15)
C10-H10C	0.98	Pd1-Cl1#1	2.3408(15)
C11-O3	1.443(7)		

C2-C1-H1A	109.5	N1-C2-C1	124.5(6)
C2-C1-H1B	109.5	C3-C2-C1	117.9(6)
H1A-C1-H1B	109.5	C8-C3-C4	119.7(6)
C2-C1-H1C	109.5	C8-C3-C2	118.9(6)
H1A-C1-H1C	109.5	C4-C3-C2	121.0(5)
H1B-C1-H1C	109.5	O1-C4-C5	124.5(6)
N1-C2-C3	117.6(5)	O1-C4-C3	115.3(5)

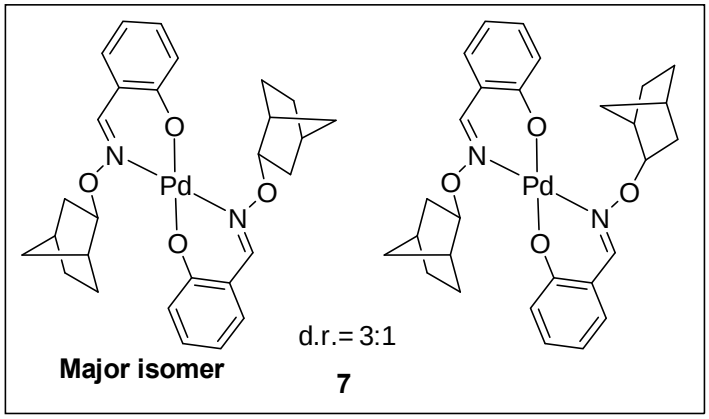
C5-C4-C3	120.2(5)	H12A-C12-H12B	108.7
C6-C5-C4	119.0(6)	C12-C13-C17	102.8(7)
C6-C5-H5	120.5	C12-C13-C14	108.6(7)
C4-C5-H5	120.5	C17-C13-C14	101.5(7)
C7-C6-C5	121.5(6)	C12-C13-H13	114.2
C7-C6-H6	119.3	C17-C13-H13	114.2
C5-C6-H6	119.3	C14-C13-H13	114.2
C6-C7-C8	120.0(6)	C13-C14-C15	102.5(7)
C6-C7-H7	120.0	C13-C14-H14A	111.3
C8-C7-H7	120.0	C15-C14-H14A	111.3
O2-C8-C3	115.1(5)	C13-C14-H14B	111.3
O2-C8-C7	125.4(5)	C15-C14-H14B	111.3
C3-C8-C7	119.4(6)	H14A-C14-H14B	109.2
O1-C9-H9A	109.5	C16-C15-C14	105.9(6)
O1-C9-H9B	109.5	C16-C15-H15A	110.6
H9A-C9-H9B	109.5	C14-C15-H15A	110.6
O1-C9-H9C	109.5	C16-C15-H15B	110.6
H9A-C9-H9C	109.5	C14-C15-H15B	110.6
H9B-C9-H9C	109.5	H15A-C15-H15B	108.7
O2-C10-H10A	109.5	C15-C16-C11	108.2(7)
O2-C10-H10B	109.5	C15-C16-C17	99.1(6)
H10A-C10-H10B	109.5	C11-C16-C17	98.6(6)
O2-C10-H10C	109.5	C15-C16-H16	116.1
H10A-C10-H10C	109.5	C11-C16-H16	116.1
H10B-C10-H10C	109.5	C17-C16-H16	116.1
O3-C11-C16	110.3(6)	C13-C17-C16	93.9(6)
O3-C11-C12	108.5(5)	C13-C17-H17A	112.9
C16-C11-C12	102.5(6)	C16-C17-H17A	112.9
O3-C11-H11	111.7	C13-C17-H17B	112.9
C16-C11-H11	111.7	C16-C17-H17B	112.9
C12-C11-H11	111.7	H17A-C17-H17B	110.4
C13-C12-C11	106.1(7)	C2-N1-O3	114.7(4)
C13-C12-H12A	110.5	C2-N1-Pd1	130.1(4)
C11-C12-H12A	110.5	O3-N1-Pd1	113.7(4)
C13-C12-H12B	110.5	C4-O1-C9	116.9(5)
C11-C12-H12B	110.5	C8-O2-C10	116.9(5)

N1-O3-C11	111.8(4)	Cl2-Pd1-Cl1	90.27(5)
Pd1-Cl1-Pd1#1	93.42(4)	N1-Pd1-Cl1#1	89.00(14)
N1-Pd1-Cl2	94.06(14)	Cl2-Pd1-Cl1#1	175.82(6)
N1-Pd1-Cl1	175.22(14)	Cl1-Pd1-Cl1#1	86.58(4)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1

X-ray structure data of Pd complex **7**:



The major diastereomer of Pd complex **7**:

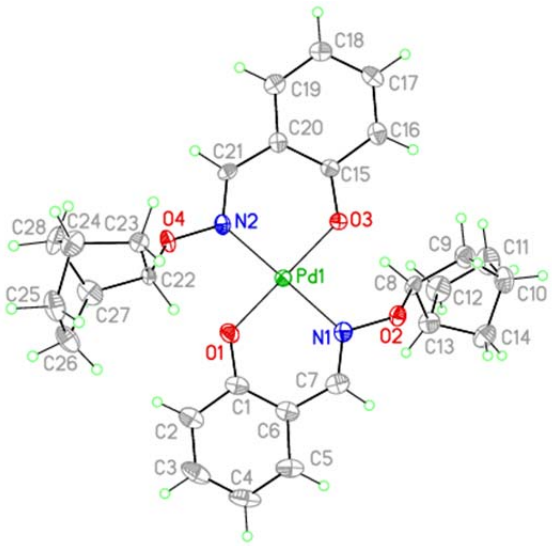


Figure S2.1. ORTEP structure of the major diastereomer of Pd complex **7** (displacement ellipsoids are scaled to the 50% probability level; all solvent molecules omitted for clarity).

The minor diastereomer of Pd complex **7**:

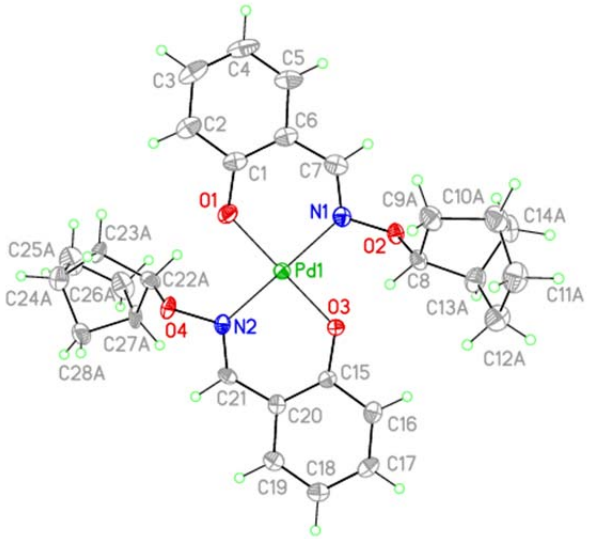


Figure S2.2. ORTEP structure of the minor diastereomer of Pd complex **7** (displacement ellipsoids are scaled to the 50% probability level; all solvent molecules omitted for clarity).

Table S2.1. Crystal data and structure refinement for Pd complex **7**.

Empirical formula	C28 H32 N2 O4 Pd
Formula weight	566.95
Temperature	100(2) K
Wavelength	0.71073 Å

Crystal system	orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 5.8758(11) Å	α= 90°.
	b = 17.966(4) Å	β= 90°.
	c = 23.513(4) Å	γ = 90°.
Volume	2482.2(8) $Å^3$	
Z	4	
Density (calculated)	1.517 Mg/m^3	
Absorption coefficient	0.785 mm^{-1}	
F(000)	1168	
Crystal size	0.230 x 0.070 x 0.040 mm^3	
Theta range for data collection	3.450 to 27.463°.	
Index ranges	-7<=h<=7, -23<=k<=23, -29<=l<=30	
Reflections collected	39216	
Independent reflections	5677 [R(int) = 0.0590]	
Completeness to theta = 25.242°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.800	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5677 / 375 / 438	
Goodness-of-fit on F^2	1.163	
Final R indices [I>2sigma(I)]	R1 = 0.0343, wR2 = 0.0650	
R indices (all data)	R1 = 0.0374, wR2 = 0.0660	
Absolute structure parameter	-0.033(15)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.419 and -0.807 $e.Å^{-3}$	

Table S2.2. Bond lengths [Å] and angles [°] for Pd complex **7**.

C1-O1	1.307(5)	C14-H14A	0.99
C1-C2	1.416(6)	C14-H14B	0.99
C1-C6	1.415(7)	C9A-C10A	1.519(18)
C2-C3	1.374(7)	C9A-H9A1	0.99
C2-H2	0.95	C9A-H9A2	0.99
C3-C4	1.380(8)	C10A-C11A	1.524(18)
C3-H3	0.95	C10A-C14A	1.528(13)
C4-C5	1.365(7)	C10A-H10A	1.00
C4-H4	0.95	C11A-C12A	1.54(3)
C5-C6	1.415(7)	C11A-H11C	0.99
C5-H5	0.95	C11A-H11D	0.99
C6-C7	1.426(7)	C12A-C13A	1.52(2)
C7-N1	1.295(6)	C12A-H12C	0.99
C7-H7	0.95	C12A-H12D	0.99
C8-O2	1.454(5)	C13A-C14A	1.507(17)
C8-C9	1.519(16)	C13A-H13A	1.00
C8-C13A	1.52(3)	C14A-H14C	0.99
C8-C9A	1.52(3)	C14A-H14D	0.99
C8-C13	1.549(15)	C15-O3	1.310(5)
C8-H8	0.96(5)	C15-C20	1.419(6)
C9-C10	1.525(13)	C15-C16	1.421(6)
C9-H9A	0.99	C16-C17	1.374(7)
C9-H9B	0.99	C16-H16	0.95
C10-C11	1.526(15)	C17-C18	1.401(7)
C10-C14	1.527(10)	C17-H17	0.95
C10-H10	1.00	C18-C19	1.371(6)
C11-C12	1.54(2)	C18-H18	0.95
C11-H11A	0.99	C19-C20	1.409(6)
C11-H11B	0.99	C19-H19	0.95
C12-C13	1.526(17)	C20-C21	1.425(6)
C12-H12A	0.99	C21-N2	1.292(6)
C12-H12B	0.99	C21-H21	0.95
C13-C14	1.507(13)	C22-O4	1.49(2)
C13-H13	1.00	C22-C27	1.52(3)

C22-C23	1.54(3)	C23A-C24A	1.54(2)
C22-H22	1.00	C23A-H23C	0.99
C23-C24	1.531(12)	C23A-H23D	0.99
C23-H23A	0.99	C24A-C25A	1.531(18)
C23-H23B	0.99	C24A-C28A	1.539(16)
C24-C25	1.523(14)	C24A-H24A	1.00
C24-C28	1.524(12)	C25A-C26A	1.55(2)
C24-H24	1.00	C25A-H25C	0.99
C25-C26	1.558(15)	C25A-H25D	0.99
C25-H25A	0.99	C26A-C27A	1.513(19)
C25-H25B	0.99	C26A-H26C	0.99
C26-C27	1.517(19)	C26A-H26D	0.99
C26-H26A	0.99	C27A-C28A	1.527(17)
C26-H26B	0.99	C27A-H27A	1.00
C27-C28	1.552(17)	C28A-H28C	0.99
C27-H27	1.00	C28A-H28D	0.99
C28-H28A	0.99	O1-Pd1	1.991(3)
C28-H28B	0.99	O2-N1	1.413(5)
C22A-O4	1.37(3)	O3-Pd1	1.988(3)
C22A-C23A	1.52(4)	O4-N2	1.412(5)
C22A-C27A	1.55(3)	Pd1-N2	2.004(3)
C22A-H22A	1.00	Pd1-N1	2.009(3)

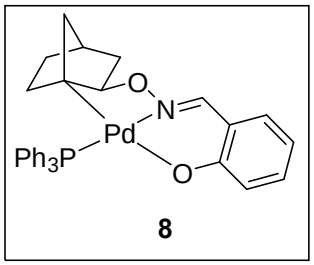
O1-C1-C2	117.7(5)	C4-C5-H5	119.2
O1-C1-C6	124.9(4)	C6-C5-H5	119.2
C2-C1-C6	117.4(5)	C1-C6-C5	119.3(5)
C3-C2-C1	121.2(6)	C1-C6-C7	124.2(5)
C3-C2-H2	119.4	C5-C6-C7	116.5(5)
C1-C2-H2	119.4	N1-C7-C6	125.3(5)
C2-C3-C4	121.3(6)	N1-C7-H7	117.3
C2-C3-H3	119.3	C6-C7-H7	117.3
C4-C3-H3	119.3	O2-C8-C9	107.2(6)
C5-C4-C3	119.2(5)	O2-C8-C13A	105.6(9)
C5-C4-H4	120.4	O2-C8-C9A	112.6(12)
C3-C4-H4	120.4	C13A-C8-C9A	104.1(8)
C4-C5-C6	121.6(6)	O2-C8-C13	110.4(6)

C9-C8-C13	103.1(6)	C13-C14-C10	96.4(8)
O2-C8-H8	106(3)	C13-C14-H14A	112.5
C9-C8-H8	113(3)	C10-C14-H14A	112.5
C13A-C8-H8	123(3)	C13-C14-H14B	112.5
C9A-C8-H8	106(3)	C10-C14-H14B	112.5
C13-C8-H8	117(3)	H14A-C14-H14B	110.0
C8-C9-C10	104.9(8)	C10A-C9A-C8	104.0(14)
C8-C9-H9A	110.8	C10A-C9A-H9A1	111.0
C10-C9-H9A	110.8	C8-C9A-H9A1	111.0
C8-C9-H9B	110.8	C10A-C9A-H9A2	111.0
C10-C9-H9B	110.8	C8-C9A-H9A2	111.0
H9A-C9-H9B	108.8	H9A1-C9A-H9A2	109.0
C11-C10-C9	107.8(9)	C9A-C10A-C11A	108.2(15)
C11-C10-C14	100.8(10)	C9A-C10A-C14A	100.1(13)
C9-C10-C14	100.1(7)	C11A-C10A-C14A	100.9(16)
C11-C10-H10	115.4	C9A-C10A-H10A	115.2
C9-C10-H10	115.4	C11A-C10A-H10A	115.2
C14-C10-H10	115.4	C14A-C10A-H10A	115.2
C10-C11-C12	103.0(8)	C10A-C11A-C12A	102.5(10)
C10-C11-H11A	111.2	C10A-C11A-H11C	111.3
C12-C11-H11A	111.2	C12A-C11A-H11C	111.3
C10-C11-H11B	111.2	C10A-C11A-H11D	111.3
C12-C11-H11B	111.2	C12A-C11A-H11D	111.3
H11A-C11-H11B	109.1	H11C-C11A-H11D	109.2
C13-C12-C11	104.4(8)	C13A-C12A-C11A	105.1(11)
C13-C12-H12A	110.9	C13A-C12A-H12C	110.7
C11-C12-H12A	110.9	C11A-C12A-H12C	110.7
C13-C12-H12B	110.9	C13A-C12A-H12D	110.7
C11-C12-H12B	110.9	C11A-C12A-H12D	110.7
H12A-C12-H12B	108.9	H12C-C12A-H12D	108.8
C14-C13-C12	100.6(9)	C14A-C13A-C8	100.5(15)
C14-C13-C8	100.9(9)	C14A-C13A-C12A	101.2(13)
C12-C13-C8	106.5(9)	C8-C13A-C12A	104.9(16)
C14-C13-H13	115.6	C14A-C13A-H13A	116.0
C12-C13-H13	115.6	C8-C13A-H13A	116.0
C8-C13-H13	115.6	C12A-C13A-H13A	116.0

C13A-C14A-C10A	96.4(11)	C24-C23-H23B	111.1
C13A-C14A-H14C	112.5	C22-C23-H23B	111.1
C10A-C14A-H14C	112.5	H23A-C23-H23B	109.0
C13A-C14A-H14D	112.5	C25-C24-C28	102.3(8)
C10A-C14A-H14D	112.5	C25-C24-C23	107.7(8)
H14C-C14A-H14D	110.0	C28-C24-C23	101.4(7)
O3-C15-C20	125.5(4)	C25-C24-H24	114.7
O3-C15-C16	116.9(4)	C28-C24-H24	114.7
C20-C15-C16	117.6(4)	C23-C24-H24	114.7
C17-C16-C15	121.2(5)	C24-C25-C26	103.5(7)
C17-C16-H16	119.4	C24-C25-H25A	111.1
C15-C16-H16	119.4	C26-C25-H25A	111.1
C16-C17-C18	121.1(5)	C24-C25-H25B	111.1
C16-C17-H17	119.5	C26-C25-H25B	111.1
C18-C17-H17	119.5	H25A-C25-H25B	109.0
C19-C18-C17	118.8(5)	C27-C26-C25	102.4(8)
C19-C18-H18	120.6	C27-C26-H26A	111.3
C17-C18-H18	120.6	C25-C26-H26A	111.3
C18-C19-C20	121.9(5)	C27-C26-H26B	111.3
C18-C19-H19	119.1	C25-C26-H26B	111.3
C20-C19-H19	119.1	H26A-C26-H26B	109.2
C19-C20-C15	119.5(4)	C26-C27-C22	108.7(15)
C19-C20-C21	116.8(4)	C26-C27-C28	102.6(10)
C15-C20-C21	123.6(4)	C22-C27-C28	101.3(14)
N2-C21-C20	125.9(4)	C26-C27-H27	114.3
N2-C21-H21	117.1	C22-C27-H27	114.3
C20-C21-H21	117.1	C28-C27-H27	114.3
O4-C22-C27	104.2(18)	C24-C28-C27	93.4(9)
O4-C22-C23	113.4(17)	C24-C28-H28A	113.0
C27-C22-C23	102.9(9)	C27-C28-H28A	113.0
O4-C22-H22	111.9	C24-C28-H28B	113.0
C27-C22-H22	111.9	C27-C28-H28B	113.0
C23-C22-H22	111.9	H28A-C28-H28B	110.4
C24-C23-C22	103.5(10)	O4-C22A-C23A	110(3)
C24-C23-H23A	111.1	O4-C22A-C27A	112(3)
C22-C23-H23A	111.1	C23A-C22A-C27A	103.2(14)

O4-C22A-H22A	110.4	C26A-C27A-C22A	109.7(17)
C23A-C22A-H22A	110.4	C28A-C27A-C22A	99.7(16)
C27A-C22A-H22A	110.4	C26A-C27A-H27A	114.8
C22A-C23A-C24A	104.7(16)	C28A-C27A-H27A	114.8
C22A-C23A-H23C	110.8	C22A-C27A-H27A	114.8
C24A-C23A-H23C	110.8	C27A-C28A-C24A	95.3(11)
C22A-C23A-H23D	110.8	C27A-C28A-H28C	112.7
C24A-C23A-H23D	110.8	C24A-C28A-H28C	112.7
H23C-C23A-H23D	108.9	C27A-C28A-H28D	112.7
C25A-C24A-C23A	108.6(15)	C24A-C28A-H28D	112.7
C25A-C24A-C28A	99.7(14)	H28C-C28A-H28D	110.2
C23A-C24A-C28A	100.5(13)	C1-O1-Pd1	126.1(3)
C25A-C24A-H24A	115.3	N1-O2-C8	110.9(3)
C23A-C24A-H24A	115.3	C15-O3-Pd1	125.7(3)
C28A-C24A-H24A	115.3	C22A-O4-N2	116.4(16)
C24A-C25A-C26A	103.4(12)	N2-O4-C22	108.6(10)
C24A-C25A-H25C	111.1	O3-Pd1-O1	178.55(13)
C26A-C25A-H25C	111.1	O3-Pd1-N2	90.95(15)
C24A-C25A-H25D	111.1	O1-Pd1-N2	89.40(15)
C26A-C25A-H25D	111.1	O3-Pd1-N1	89.27(15)
H25C-C25A-H25D	109.0	O1-Pd1-N1	90.41(16)
C27A-C26A-C25A	103.7(11)	N2-Pd1-N1	178.48(16)
C27A-C26A-H26C	111.0	C7-N1-O2	113.1(3)
C25A-C26A-H26C	111.0	C7-N1-Pd1	125.7(4)
C27A-C26A-H26D	111.0	O2-N1-Pd1	119.8(3)
C25A-C26A-H26D	111.0	C21-N2-O4	112.7(3)
H26C-C26A-H26D	109.0	C21-N2-Pd1	125.7(3)
C26A-C27A-C28A	101.4(11)	O4-N2-Pd1	120.3(3)

X-ray structure data of Pd complex **8**:



8

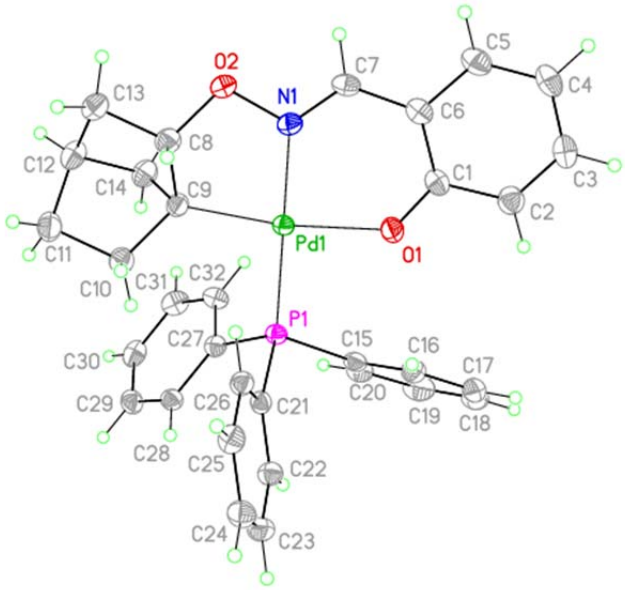


Figure S3. ORTEP structure of Pd complex **8** (displacement ellipsoids are scaled to the 50% probability level; all solvent molecules omitted for clarity).

Table S3.1. Crystal data and structure refinement for Pd complex **8**.

Empirical formula	C32 H30 N O2 P Pd	
Formula weight	597.94	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.1130(9) Å	α= 109.376(3)°.
	b = 11.3390(11) Å	β= 105.198(4)°.
	c = 13.8100(12) Å	γ = 93.408(3)°.
Volume	1282.2(2) Å^3	
Z	2	

Density (calculated)	1.549 Mg/m^3
Absorption coefficient	6.669 mm^{-1}
F(000)	612
Crystal size	0.190 x 0.100 x 0.067 mm^3
Theta range for data collection	3.556 to 76.893°.
Index ranges	-10<=h<=11, -13<=k<=14, -17<=l<=16
Reflections collected	15182
Independent reflections	5283 [R(int) = 0.0188]
Completeness to theta = 67.684°	100.0 %
Absorption correction	Gaussian
Max. and min. transmission	0.689 and 0.459
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5283 / 0 / 334
Goodness-of-fit on F^2	1.080
Final R indices [I>2sigma(I)]	R1 = 0.0207, wR2 = 0.0543
R indices (all data)	R1 = 0.0210, wR2 = 0.0544
Extinction coefficient	n/a
Largest diff. peak and hole	0.410 and -0.498 $e.Å^{-3}$

Table S3.2. Bond lengths [Å] and angles [°] for Pd complex **8**.

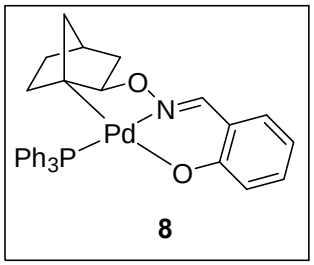
C1-O1	1.297(2)	C15-C20	1.390(3)
C1-C2	1.422(3)	C15-C16	1.397(3)
C1-C6	1.426(3)	C15-P1	1.8282(18)
C2-C3	1.372(3)	C16-C17	1.384(3)
C2-H2	0.95	C16-H16	0.95
C3-C4	1.389(3)	C17-C18	1.379(3)
C3-H3	0.95	C17-H17	0.95
C4-C5	1.369(3)	C18-C19	1.385(4)
C4-H4	0.95	C18-H18	0.95
C5-C6	1.414(3)	C19-C20	1.398(3)
C5-H5	0.95	C19-H19	0.95
C6-C7	1.435(3)	C20-H20	0.95
C7-N1	1.285(2)	C21-C26	1.395(2)
C7-H7	0.95	C21-C22	1.396(2)
C8-O2	1.453(2)	C21-P1	1.8195(17)
C8-C13	1.537(3)	C22-C23	1.387(3)
C8-C9	1.548(2)	C22-H22	0.95
C8-H8	1.00	C23-C24	1.387(3)
C9-C10	1.528(2)	C23-H23	0.95
C9-C14	1.543(2)	C24-C25	1.384(3)
C9-Pd1	2.0404(17)	C24-H24	0.95
C10-C11	1.565(3)	C25-C26	1.390(2)
C10-H10A	0.99	C25-H25	0.95
C10-H10B	0.99	C26-H26	0.95
C11-C12	1.525(3)	C27-C32	1.392(2)
C11-H11A	0.99	C27-C28	1.395(2)
C11-H11B	0.99	C27-P1	1.8168(18)
C12-C13	1.540(3)	C28-C29	1.391(3)
C12-C14	1.544(3)	C28-H28	0.95
C12-H12	1.00	C29-C30	1.386(3)
C13-H13A	0.99	C29-H29	0.95
C13-H13B	0.99	C30-C31	1.378(3)
C14-H14A	0.99	C30-H30	0.95
C14-H14B	0.99	C31-C32	1.387(3)

C31-H31	0.95	N1-Pd1	2.0149(15)
C32-H32	0.95	O1-Pd1	2.0682(13)
N1-O2	1.4099(19)	Pd1-P1	2.2549(5)

O1-C1-C2	117.37(17)	C8-C9-Pd1	104.21(11)
O1-C1-C6	125.53(17)	C9-C10-C11	104.27(15)
C2-C1-C6	117.09(17)	C9-C10-H10A	110.9
C3-C2-C1	121.77(19)	C11-C10-H10A	110.9
C3-C2-H2	119.1	C9-C10-H10B	110.9
C1-C2-H2	119.1	C11-C10-H10B	110.9
C2-C3-C4	121.02(19)	H10A-C10-H10B	108.9
C2-C3-H3	119.5	C12-C11-C10	102.44(15)
C4-C3-H3	119.5	C12-C11-H11A	111.3
C5-C4-C3	118.91(18)	C10-C11-H11A	111.3
C5-C4-H4	120.5	C12-C11-H11B	111.3
C3-C4-H4	120.5	C10-C11-H11B	111.3
C4-C5-C6	122.24(19)	H11A-C11-H11B	109.2
C4-C5-H5	118.9	C11-C12-C13	108.04(17)
C6-C5-H5	118.9	C11-C12-C14	101.98(16)
C5-C6-C1	118.94(18)	C13-C12-C14	101.46(16)
C5-C6-C7	116.82(17)	C11-C12-H12	114.6
C1-C6-C7	124.24(16)	C13-C12-H12	114.6
N1-C7-C6	124.64(17)	C14-C12-H12	114.6
N1-C7-H7	117.7	C8-C13-C12	103.13(15)
C6-C7-H7	117.7	C8-C13-H13A	111.1
O2-C8-C13	106.90(15)	C12-C13-H13A	111.1
O2-C8-C9	111.26(14)	C8-C13-H13B	111.1
C13-C8-C9	104.40(15)	C12-C13-H13B	111.1
O2-C8-H8	111.3	H13A-C13-H13B	109.1
C13-C8-H8	111.3	C9-C14-C12	94.81(14)
C9-C8-H8	111.3	C9-C14-H14A	112.8
C10-C9-C14	101.84(15)	C12-C14-H14A	112.8
C10-C9-C8	105.77(14)	C9-C14-H14B	112.8
C14-C9-C8	100.28(14)	C12-C14-H14B	112.8
C10-C9-Pd1	122.86(13)	H14A-C14-H14B	110.2
C14-C9-Pd1	119.02(12)	C20-C15-C16	119.27(17)

C20-C15-P1	123.63(15)	C32-C27-C28	118.87(16)
C16-C15-P1	117.05(14)	C32-C27-P1	116.00(13)
C17-C16-C15	120.57(19)	C28-C27-P1	125.13(14)
C17-C16-H16	119.7	C29-C28-C27	119.96(17)
C15-C16-H16	119.7	C29-C28-H28	120.0
C18-C17-C16	120.1(2)	C27-C28-H28	120.0
C18-C17-H17	119.9	C30-C29-C28	120.33(17)
C16-C17-H17	119.9	C30-C29-H29	119.8
C17-C18-C19	120.00(19)	C28-C29-H29	119.8
C17-C18-H18	120.0	C31-C30-C29	120.08(18)
C19-C18-H18	120.0	C31-C30-H30	120.0
C18-C19-C20	120.3(2)	C29-C30-H30	120.0
C18-C19-H19	119.8	C30-C31-C32	119.77(18)
C20-C19-H19	119.8	C30-C31-H31	120.1
C15-C20-C19	119.7(2)	C32-C31-H31	120.1
C15-C20-H20	120.1	C31-C32-C27	120.99(17)
C19-C20-H20	120.1	C31-C32-H32	119.5
C26-C21-C22	119.32(16)	C27-C32-H32	119.5
C26-C21-P1	119.13(13)	C7-N1-O2	114.50(14)
C22-C21-P1	121.45(13)	C7-N1-Pd1	129.45(13)
C23-C22-C21	120.17(17)	O2-N1-Pd1	115.92(10)
C23-C22-H22	119.9	C1-O1-Pd1	126.70(12)
C21-C22-H22	119.9	N1-O2-C8	106.50(13)
C24-C23-C22	119.94(18)	N1-Pd1-C9	82.31(7)
C24-C23-H23	120.0	N1-Pd1-O1	88.86(6)
C22-C23-H23	120.0	C9-Pd1-O1	171.17(6)
C25-C24-C23	120.47(17)	N1-Pd1-P1	178.82(4)
C25-C24-H24	119.8	C9-Pd1-P1	97.51(5)
C23-C24-H24	119.8	O1-Pd1-P1	91.31(4)
C24-C25-C26	119.72(17)	C27-P1-C21	107.88(8)
C24-C25-H25	120.1	C27-P1-C15	103.40(8)
C26-C25-H25	120.1	C21-P1-C15	102.57(8)
C25-C26-C21	120.37(17)	C27-P1-Pd1	116.39(6)
C25-C26-H26	119.8	C21-P1-Pd1	112.49(6)
C21-C26-H26	119.8	C15-P1-Pd1	112.86(6)

X-ray structure data of Pd complex **10**:



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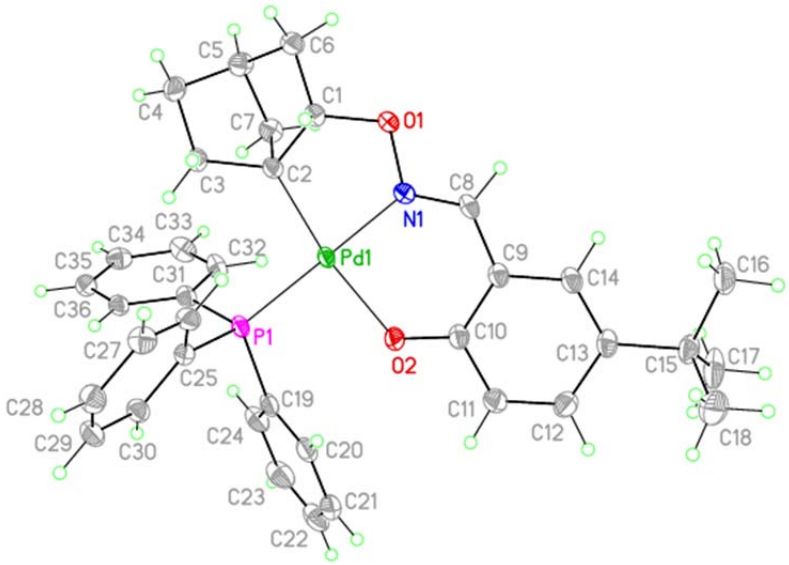


Figure S4. ORTEP structure of Pd complex **10** (displacement ellipsoids are scaled to the 50% probability level; all solvent molecules omitted for clarity).

Table S4.1. Crystal data and structure refinement for Pd complex **10**.

Empirical formula	C42 H52 N O2 P Pd	
Formula weight	740.21	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.224(2) Å	α= 105.095(3)°.
	b = 11.291(2) Å	β= 99.285(3)°.
	c = 18.410(3) Å	γ = 92.776(3)°.
Volume	1818.7(6) Å^3	
Z	2	

Density (calculated)	1.352 Mg/m^3
Absorption coefficient	4.802 mm^{-1}
F(000)	776
Crystal size	0.170 x 0.120 x 0.050 mm^3
Theta range for data collection	2.527 to 74.418°.
Index ranges	-11<=h<=11, -14<=k<=14, -22<=l<=22
Reflections collected	33905
Independent reflections	7207 [R(int) = 0.0262]
Completeness to theta = 67.684°	99.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00 and 0.813
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7207 / 35 / 427
Goodness-of-fit on F^2	1.039
Final R indices [I>2sigma(I)]	R1 = 0.0236, wR2 = 0.0593
R indices (all data)	R1 = 0.0238, wR2 = 0.0595
Extinction coefficient	n/a
Largest diff. peak and hole	0.506 and -0.653 $e.Å^{-3}$

Table S4.2. Bond lengths [Å] and angles [°] for Pd complex **10**.

C1-O1	1.451(2)	C15-C17	1.527(3)
C1-C6	1.544(2)	C15-C16	1.530(3)
C1-C2	1.550(2)	C15-C18	1.542(3)
C1-H1	1.0000	C16-H16A	0.98
C2-C3	1.541(2)	C16-H16B	0.98
C2-C7	1.546(2)	C16-H16C	0.98
C2-Pd1	2.0412(17)	C17-H17A	0.98
C3-C4	1.560(2)	C17-H17B	0.98
C3-H3A	0.99	C17-H17C	0.98
C3-H3B	0.99	C18-H18A	0.98
C4-C5	1.534(3)	C18-H18B	0.98
C4-H4A	0.99	C18-H18C	0.98
C4-H4B	0.99	C19-C20	1.391(3)
C5-C6	1.539(2)	C19-C24	1.403(3)
C5-C7	1.546(3)	C19-P1	1.8323(19)
C5-H5	1.00	C20-C21	1.388(3)
C6-H6A	0.99	C20-H20	0.95
C6-H6B	0.99	C21-C22	1.391(3)
C7-H7A	0.99	C21-H21	0.95
C7-H7B	0.99	C22-C23	1.369(4)
C8-N1	1.288(2)	C22-H22	0.95
C8-C9	1.435(3)	C23-C24	1.390(3)
C8-H8	0.95	C23-H23	0.95
C9-C14	1.420(2)	C24-H24	0.95
C9-C10	1.430(2)	C25-C26	1.396(2)
C10-O2	1.300(2)	C25-C30	1.400(2)
C10-C11	1.420(3)	C25-P1	1.8244(18)
C11-C12	1.372(3)	C26-C27	1.391(3)
C11-H11	0.95	C26-H26	0.95
C12-C13	1.413(3)	C27-C28	1.385(3)
C12-H12	0.95	C27-H27	0.95
C13-C14	1.375(3)	C28-C29	1.392(3)
C13-C15	1.536(2)	C28-H28	0.95
C14-H14	0.95	C29-C30	1.390(3)

C29-H29	0.95	C41-H41A	0.99
C30-H30	0.95	C41-H41B	0.99
C31-C36	1.389(2)	C42-H42A	0.98
C31-C32	1.399(2)	C42-H42B	0.98
C31-P1	1.8237(18)	C42-H42C	0.98
C32-C33	1.385(3)	C37A-C38A	1.584(8)
C32-H32	0.95	C37A-H37D	0.98
C33-C34	1.381(3)	C37A-H37E	0.98
C33-H33	0.95	C37A-H37F	0.98
C34-C35	1.387(3)	C38A-C39A	1.484(8)
C34-H34	0.95	C38A-H38C	0.99
C35-C36	1.392(3)	C38A-H38D	0.99
C35-H35	0.95	C39A-C40A	1.506(8)
C36-H36	0.95	C39A-H39C	0.99
C37-C38	1.556(5)	C39A-H39D	0.99
C37-H37A	0.98	C40A-C41A	1.532(8)
C37-H37B	0.98	C40A-H40C	0.99
C37-H37C	0.98	C40A-H40D	0.99
C38-C39	1.497(5)	C41A-C42A	1.609(8)
C38-H38A	0.99	C41A-H41C	0.99
C38-H38B	0.99	C41A-H41D	0.99
C39-C40	1.510(5)	C42A-H42D	0.98
C39-H39A	0.99	C42A-H42E	0.98
C39-H39B	0.99	C42A-H42F	0.98
C40-C41	1.514(4)	N1-O1	1.4102(18)
C40-H40A	0.99	N1-Pd1	2.0206(14)
C40-H40B	0.99	O2-Pd1	2.0844(13)
C41-C42	1.576(5)	P1-Pd1	2.2637(5)

O1-C1-C6	106.74(14)	C3-C2-C1	105.11(14)
O1-C1-C2	111.21(14)	C7-C2-C1	100.16(13)
C6-C1-C2	104.94(13)	C3-C2-Pd1	122.89(12)
O1-C1-H1	111.2	C7-C2-Pd1	119.90(12)
C6-C1-H1	111.2	C1-C2-Pd1	104.16(11)
C2-C1-H1	111.2	C2-C3-C4	104.33(14)
C3-C2-C7	101.55(14)	C2-C3-H3A	110.9

C4-C3-H3A	110.9	C11-C10-C9	115.95(16)
C2-C3-H3B	110.9	C12-C11-C10	122.58(17)
C4-C3-H3B	110.9	C12-C11-H11	118.7
H3A-C3-H3B	108.9	C10-C11-H11	118.7
C5-C4-C3	102.69(14)	C11-C12-C13	122.01(17)
C5-C4-H4A	111.2	C11-C12-H12	119.0
C3-C4-H4A	111.2	C13-C12-H12	119.0
C5-C4-H4B	111.2	C14-C13-C12	116.34(16)
C3-C4-H4B	111.2	C14-C13-C15	123.35(17)
H4A-C4-H4B	109.1	C12-C13-C15	120.20(17)
C4-C5-C6	108.03(15)	C13-C14-C9	123.52(16)
C4-C5-C7	101.72(14)	C13-C14-H14	118.2
C6-C5-C7	101.92(14)	C9-C14-H14	118.2
C4-C5-H5	114.6	C17-C15-C16	109.26(18)
C6-C5-H5	114.6	C17-C15-C13	108.05(15)
C7-C5-H5	114.6	C16-C15-C13	111.99(16)
C5-C6-C1	102.64(14)	C17-C15-C18	110.30(19)
C5-C6-H6A	111.2	C16-C15-C18	106.82(17)
C1-C6-H6A	111.2	C13-C15-C18	110.42(17)
C5-C6-H6B	111.2	C15-C16-H16A	109.5
C1-C6-H6B	111.2	C15-C16-H16B	109.5
H6A-C6-H6B	109.2	H16A-C16-H16B	109.5
C5-C7-C2	95.03(13)	C15-C16-H16C	109.5
C5-C7-H7A	112.7	H16A-C16-H16C	109.5
C2-C7-H7A	112.7	H16B-C16-H16C	109.5
C5-C7-H7B	112.7	C15-C17-H17A	109.5
C2-C7-H7B	112.7	C15-C17-H17B	109.5
H7A-C7-H7B	110.2	H17A-C17-H17B	109.5
N1-C8-C9	124.70(15)	C15-C17-H17C	109.5
N1-C8-H8	117.6	H17A-C17-H17C	109.5
C9-C8-H8	117.6	H17B-C17-H17C	109.5
C14-C9-C10	119.52(16)	C15-C18-H18A	109.5
C14-C9-C8	116.65(15)	C15-C18-H18B	109.5
C10-C9-C8	123.77(16)	H18A-C18-H18B	109.5
O2-C10-C11	118.20(16)	C15-C18-H18C	109.5
O2-C10-C9	125.85(16)	H18A-C18-H18C	109.5

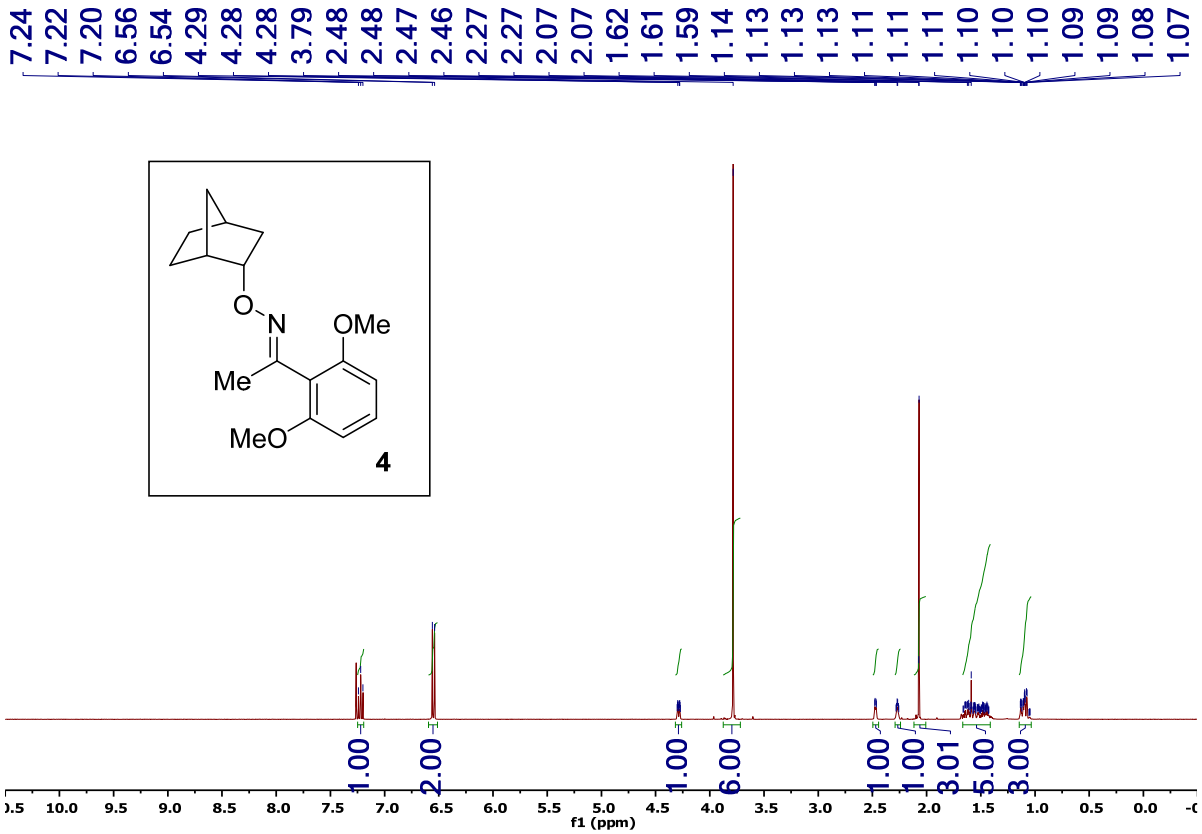
H18B-C18-H18C	109.5	C25-C30-H30	119.8
C20-C19-C24	119.14(18)	C36-C31-C32	118.91(16)
C20-C19-P1	118.52(14)	C36-C31-P1	124.32(13)
C24-C19-P1	122.32(16)	C32-C31-P1	116.66(14)
C21-C20-C19	120.0(2)	C33-C32-C31	120.83(17)
C21-C20-H20	120.0	C33-C32-H32	119.6
C19-C20-H20	120.0	C31-C32-H32	119.6
C20-C21-C22	120.0(2)	C34-C33-C32	119.94(17)
C20-C21-H21	120.0	C34-C33-H33	120.0
C22-C21-H21	120.0	C32-C33-H33	120.0
C23-C22-C21	120.7(2)	C33-C34-C35	119.79(17)
C23-C22-H22	119.6	C33-C34-H34	120.1
C21-C22-H22	119.6	C35-C34-H34	120.1
C22-C23-C24	119.7(2)	C34-C35-C36	120.54(17)
C22-C23-H23	120.2	C34-C35-H35	119.7
C24-C23-H23	120.2	C36-C35-H35	119.7
C23-C24-C19	120.5(2)	C31-C36-C35	119.98(16)
C23-C24-H24	119.8	C31-C36-H36	120.0
C19-C24-H24	119.8	C35-C36-H36	120.0
C26-C25-C30	118.97(16)	C38-C37-H37A	109.5
C26-C25-P1	118.93(13)	C38-C37-H37B	109.5
C30-C25-P1	122.07(13)	H37A-C37-H37B	109.5
C27-C26-C25	120.44(16)	C38-C37-H37C	109.5
C27-C26-H26	119.8	H37A-C37-H37C	109.5
C25-C26-H26	119.8	H37B-C37-H37C	109.5
C28-C27-C26	120.21(17)	C39-C38-C37	110.9(3)
C28-C27-H27	119.9	C39-C38-H38A	109.5
C26-C27-H27	119.9	C37-C38-H38A	109.5
C27-C28-C29	119.91(17)	C39-C38-H38B	109.5
C27-C28-H28	120.0	C37-C38-H38B	109.5
C29-C28-H28	120.0	H38A-C38-H38B	108.1
C30-C29-C28	120.08(17)	C38-C39-C40	114.1(3)
C30-C29-H29	120.0	C38-C39-H39A	108.7
C28-C29-H29	120.0	C40-C39-H39A	108.7
C29-C30-C25	120.38(16)	C38-C39-H39B	108.7
C29-C30-H30	119.8	C40-C39-H39B	108.7

H39A-C39-H39B	107.6	H39C-C39A-H39D	107.2
C39-C40-C41	114.9(3)	C39A-C40A-C41A	116.7(7)
C39-C40-H40A	108.5	C39A-C40A-H40C	108.1
C41-C40-H40A	108.5	C41A-C40A-H40C	108.1
C39-C40-H40B	108.5	C39A-C40A-H40D	108.1
C41-C40-H40B	108.5	C41A-C40A-H40D	108.1
H40A-C40-H40B	107.5	H40C-C40A-H40D	107.3
C40-C41-C42	108.7(3)	C40A-C41A-C42A	104.9(7)
C40-C41-H41A	109.9	C40A-C41A-H41C	110.8
C42-C41-H41A	109.9	C42A-C41A-H41C	110.8
C40-C41-H41B	109.9	C40A-C41A-H41D	110.8
C42-C41-H41B	109.9	C42A-C41A-H41D	110.8
H41A-C41-H41B	108.3	H41C-C41A-H41D	108.8
C41-C42-H42A	109.5	C41A-C42A-H42D	109.5
C41-C42-H42B	109.5	C41A-C42A-H42E	109.5
H42A-C42-H42B	109.5	H42D-C42A-H42E	109.5
C41-C42-H42C	109.5	C41A-C42A-H42F	109.5
H42A-C42-H42C	109.5	H42D-C42A-H42F	109.5
H42B-C42-H42C	109.5	H42E-C42A-H42F	109.5
C38A-C37A-H37D	109.5	C8-N1-O1	114.02(13)
C38A-C37A-H37E	109.5	C8-N1-Pd1	130.19(12)
H37D-C37A-H37E	109.5	O1-N1-Pd1	115.61(10)
C38A-C37A-H37F	109.5	N1-O1-C1	106.60(12)
H37D-C37A-H37F	109.5	C10-O2-Pd1	126.78(11)
H37E-C37A-H37F	109.5	C31-P1-C25	106.97(8)
C39A-C38A-C37A	114.7(7)	C31-P1-C19	102.01(8)
C39A-C38A-H38C	108.6	C25-P1-C19	103.34(8)
C37A-C38A-H38C	108.6	C31-P1-Pd1	117.55(6)
C39A-C38A-H38D	108.6	C25-P1-Pd1	112.13(6)
C37A-C38A-H38D	108.6	C19-P1-Pd1	113.45(6)
H38C-C38A-H38D	107.6	N1-Pd1-C2	82.32(6)
C38A-C39A-C40A	117.8(8)	N1-Pd1-O2	88.15(5)
C38A-C39A-H39C	107.8	C2-Pd1-O2	170.43(6)
C40A-C39A-H39C	107.8	N1-Pd1-P1	178.95(4)
C38A-C39A-H39D	107.8	C2-Pd1-P1	97.30(5)
C40A-C39A-H39D	107.8	O2-Pd1-P1	92.21(4)

VI. References

1. Ren, Z.; Mo, F.; Dong, G. *J. Am. Chem. Soc.* **2012,** *134*, 16991-16994.

VII. Spectra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OMe
Me
MeO
4
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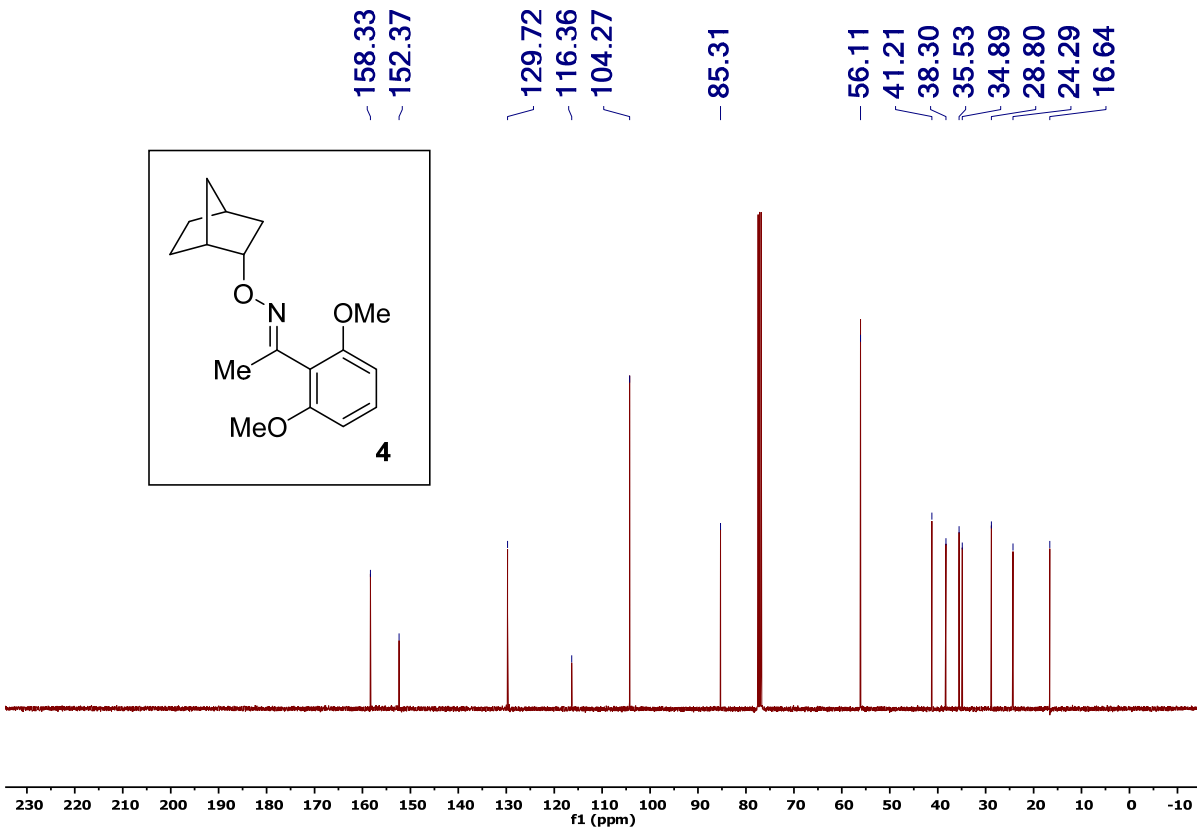
f1 (ppm)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Me
MeO
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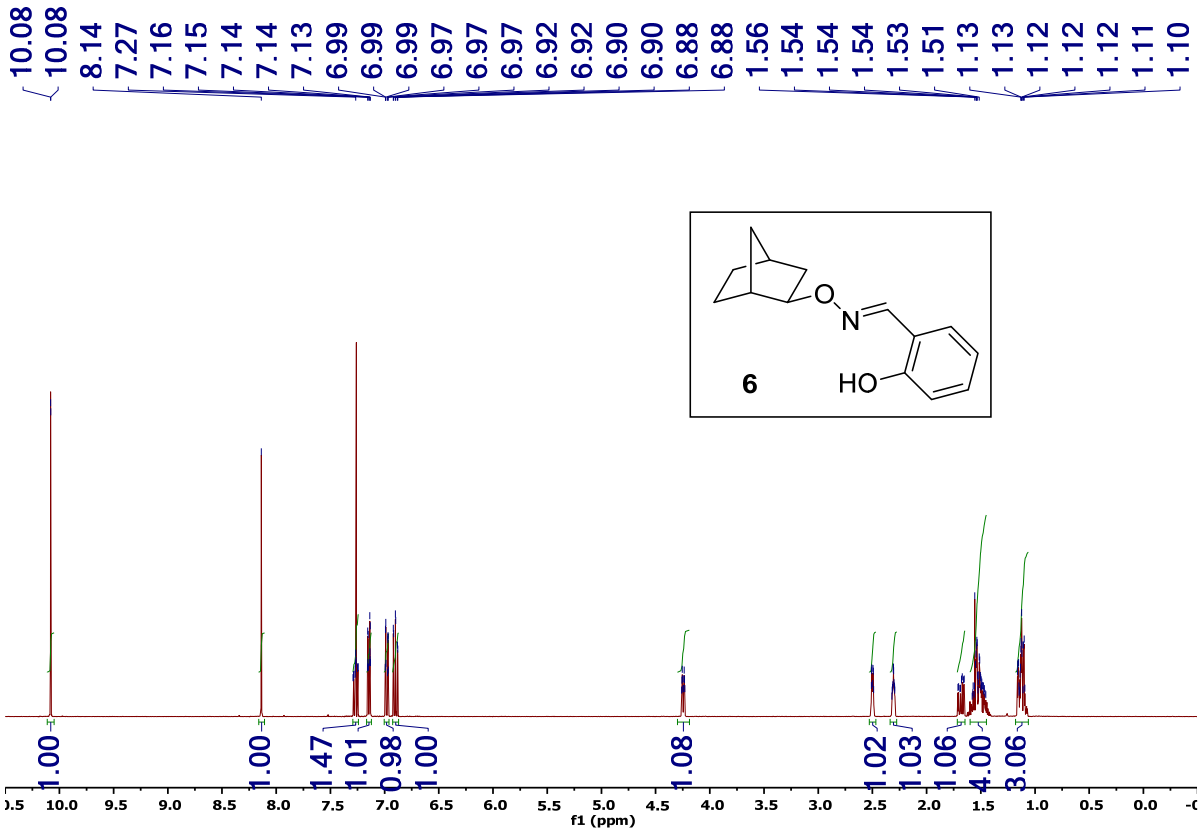
f1 (ppm)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6.97
6.97
6.92
6.92
6.90
6.90
6.88
6.88
1.56
1.54
1.54
1.54
1.53
1.51
1.13
1.13
1.12
1.12
1.12
1.11
1.10
O
N
6
HO
1.00
1.00
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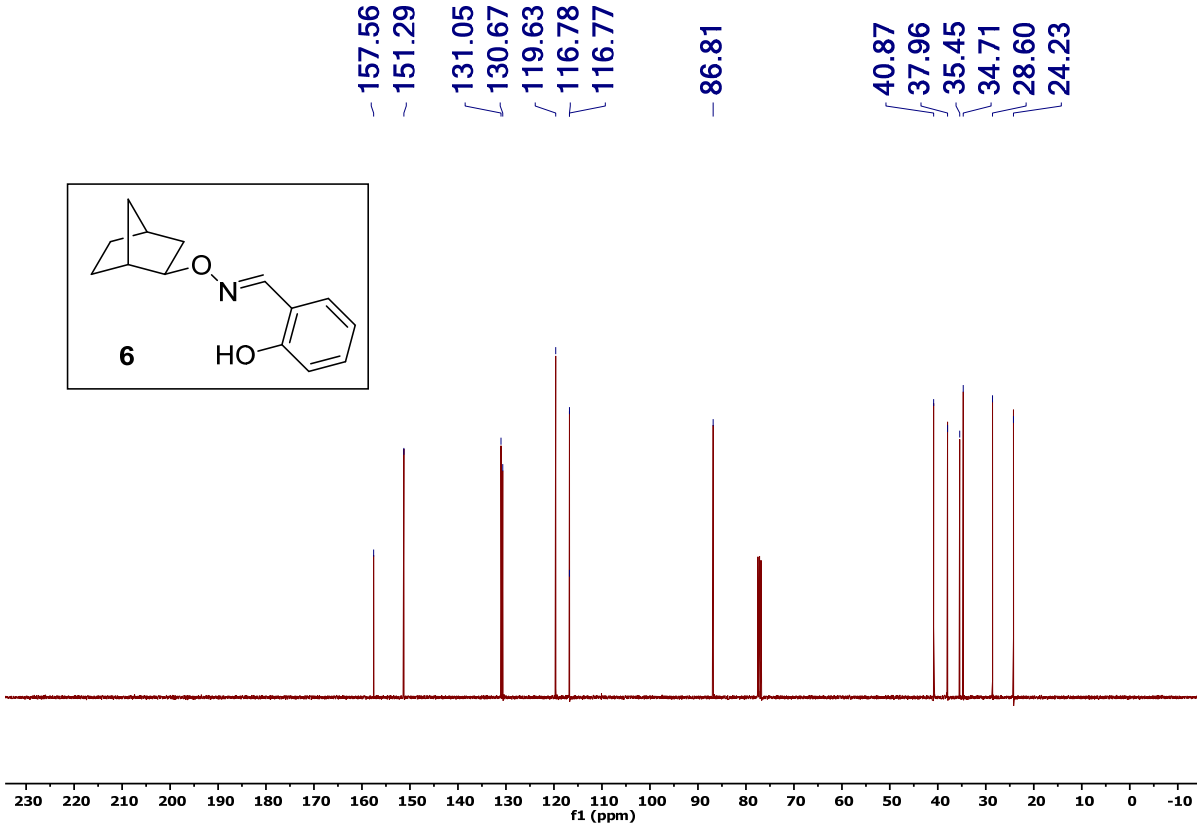
3.06
f1 (ppm)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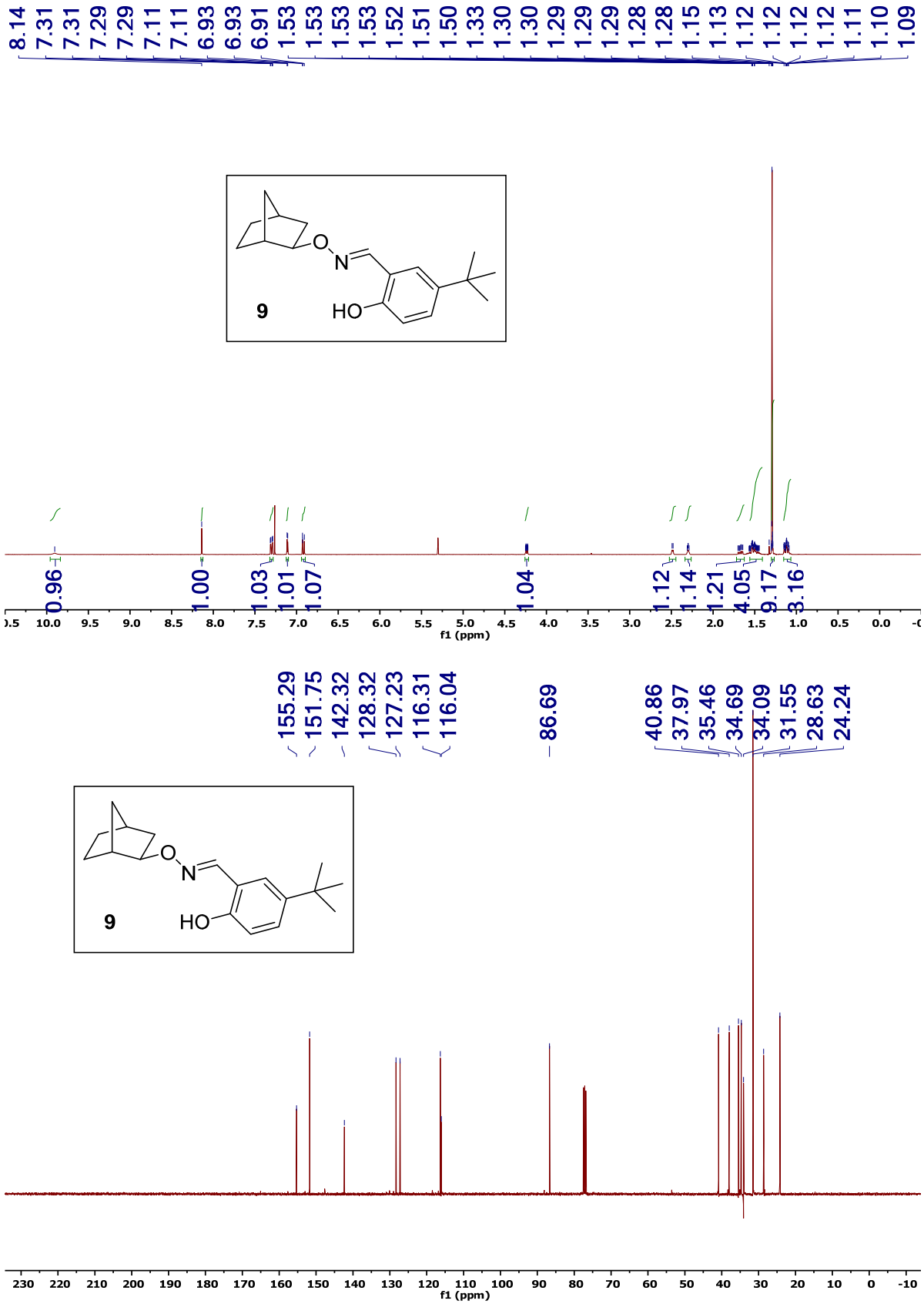
24.23
O
N
6
HO
f1 (ppm)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9
HO
0.96 1.00 1.03 1.01 1.07 1.04 1.12 1.14 1.21 4.05 9.17 3.16
f1 (ppm)
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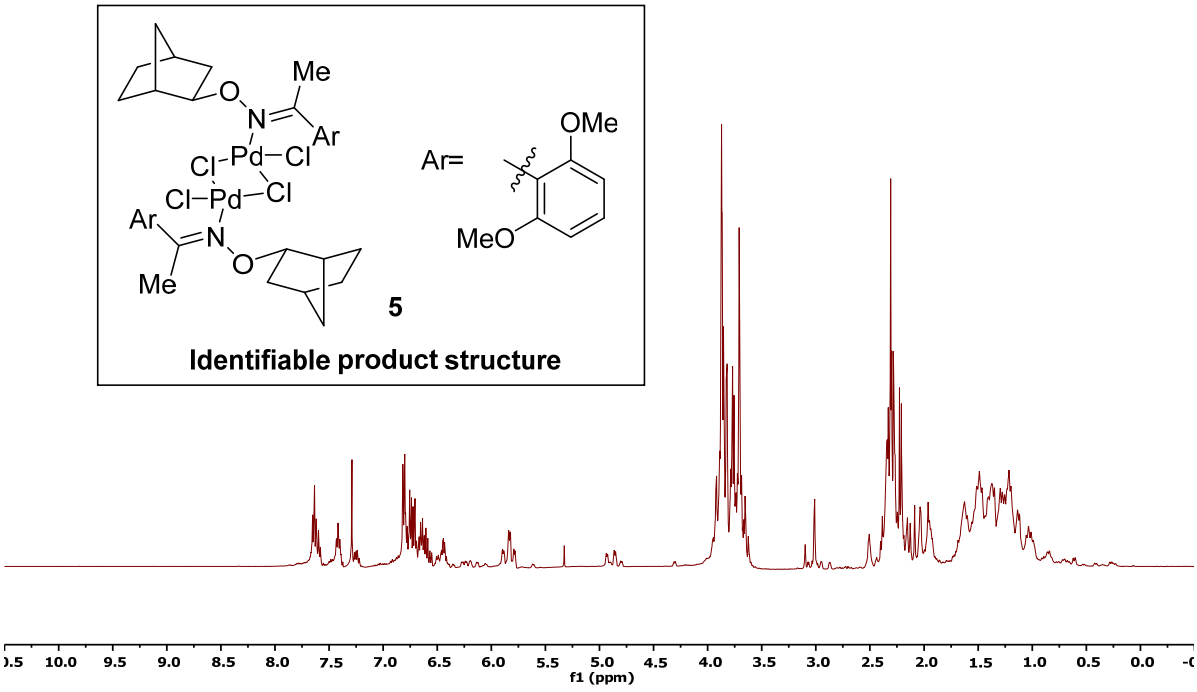
9
HO
f1 (ppm)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Cl–Pd–Cl
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O
Me
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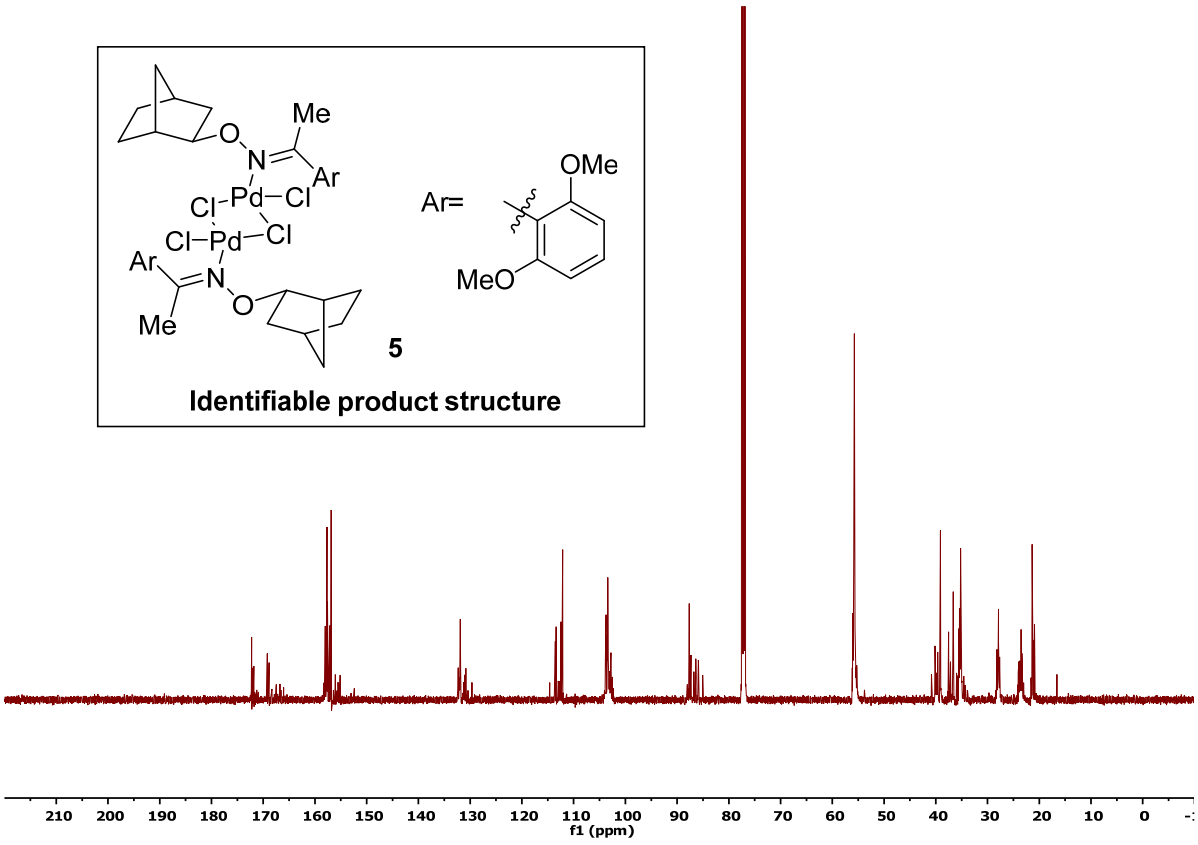
Ar=
OMe
MeO
Identifiable product structure
f1 (ppm)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Cl–Pd–Cl
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Ar=
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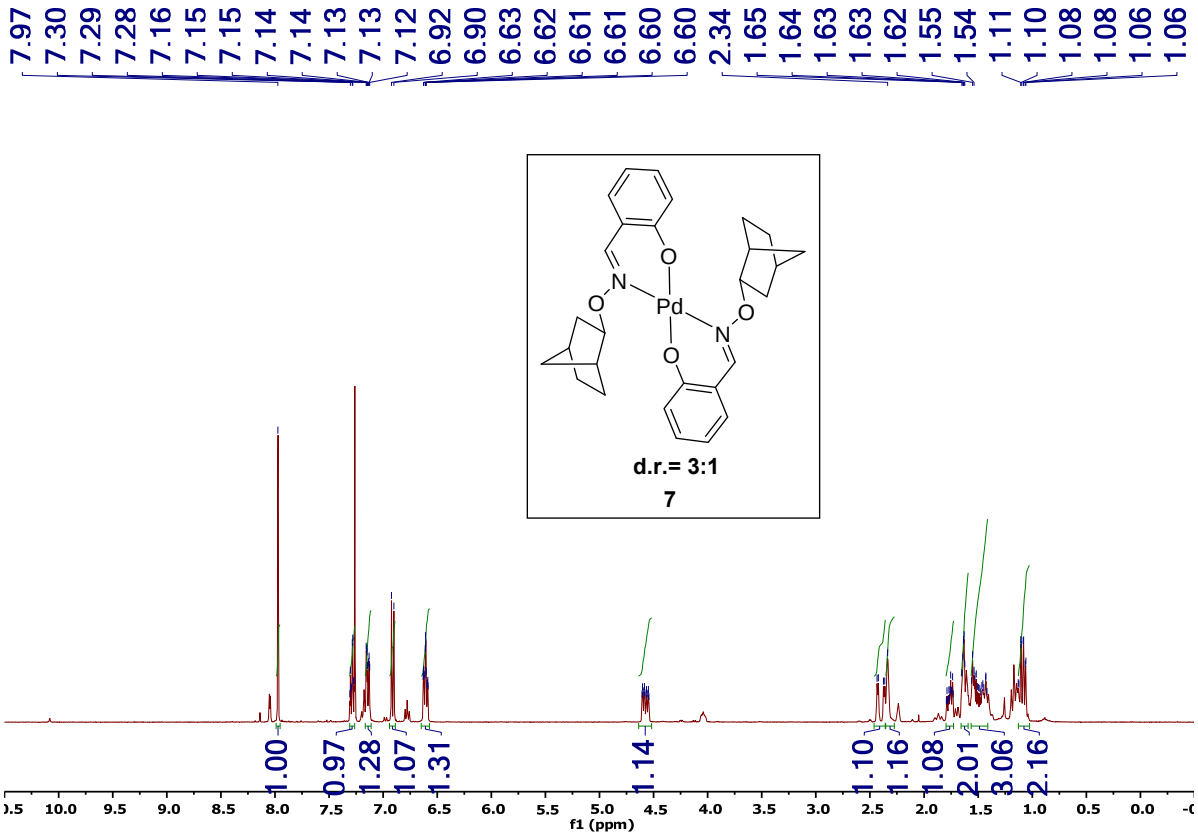
Identifiable product structure
f1 (ppm)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7.12
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1.62
1.55
1.54
1.11
1.10
1.08
1.08
1.06
1.06
d.r.= 3:1
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1.31
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1.10
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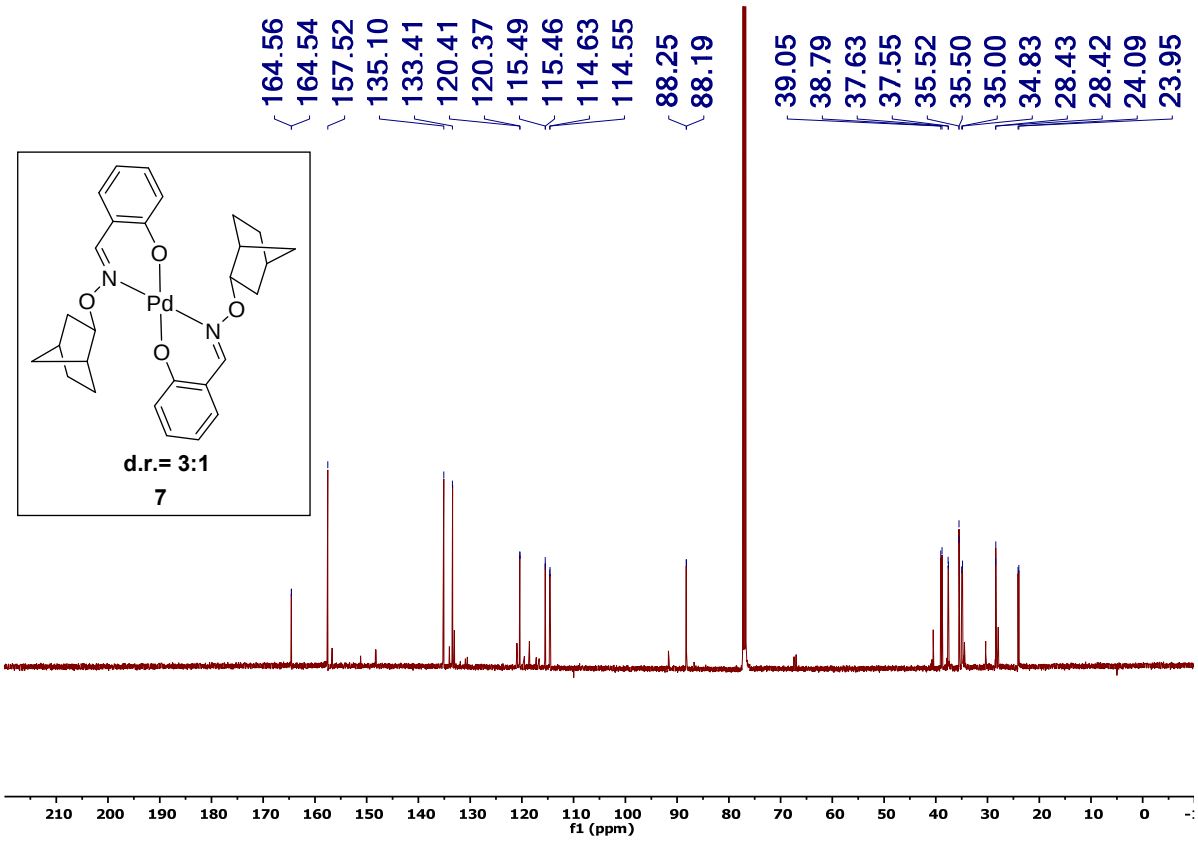
2.01
3.06
2.16
f1 (ppm)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114.63
114.55
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38.79
37.63
37.55
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23.95
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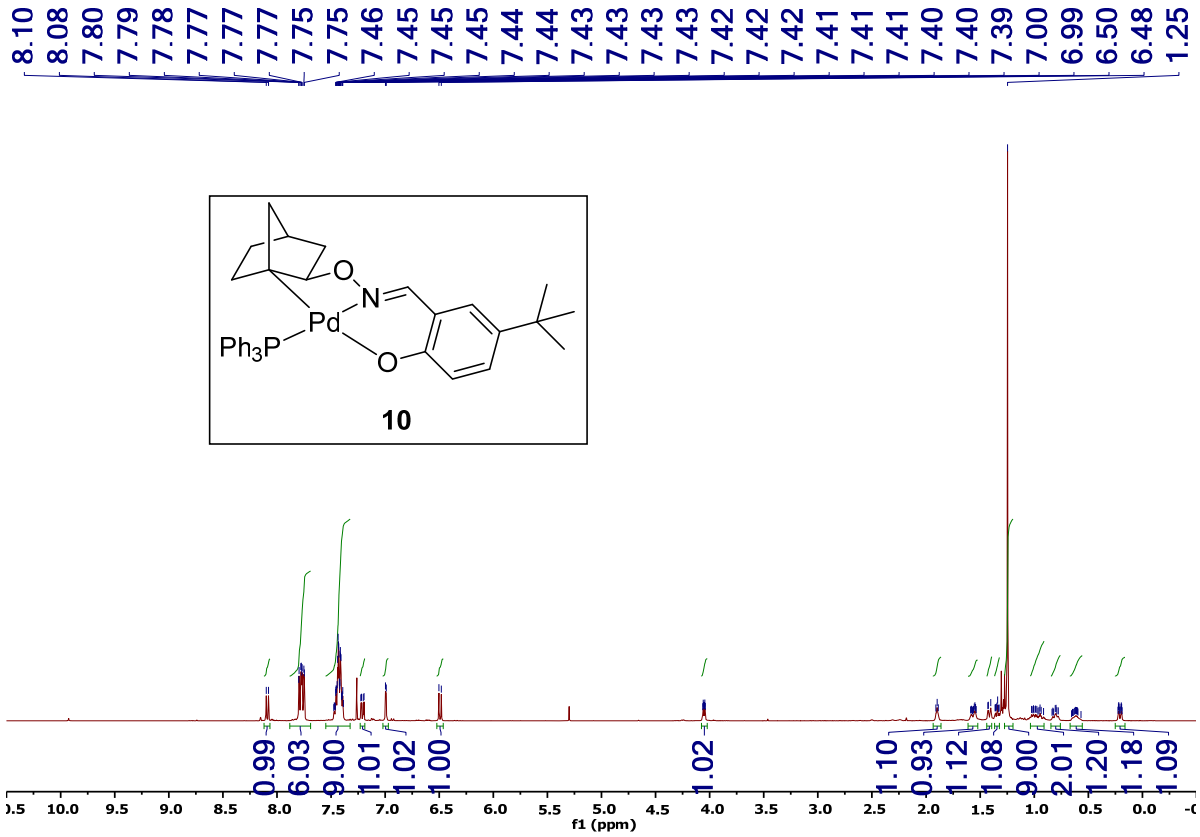
f1 (ppm)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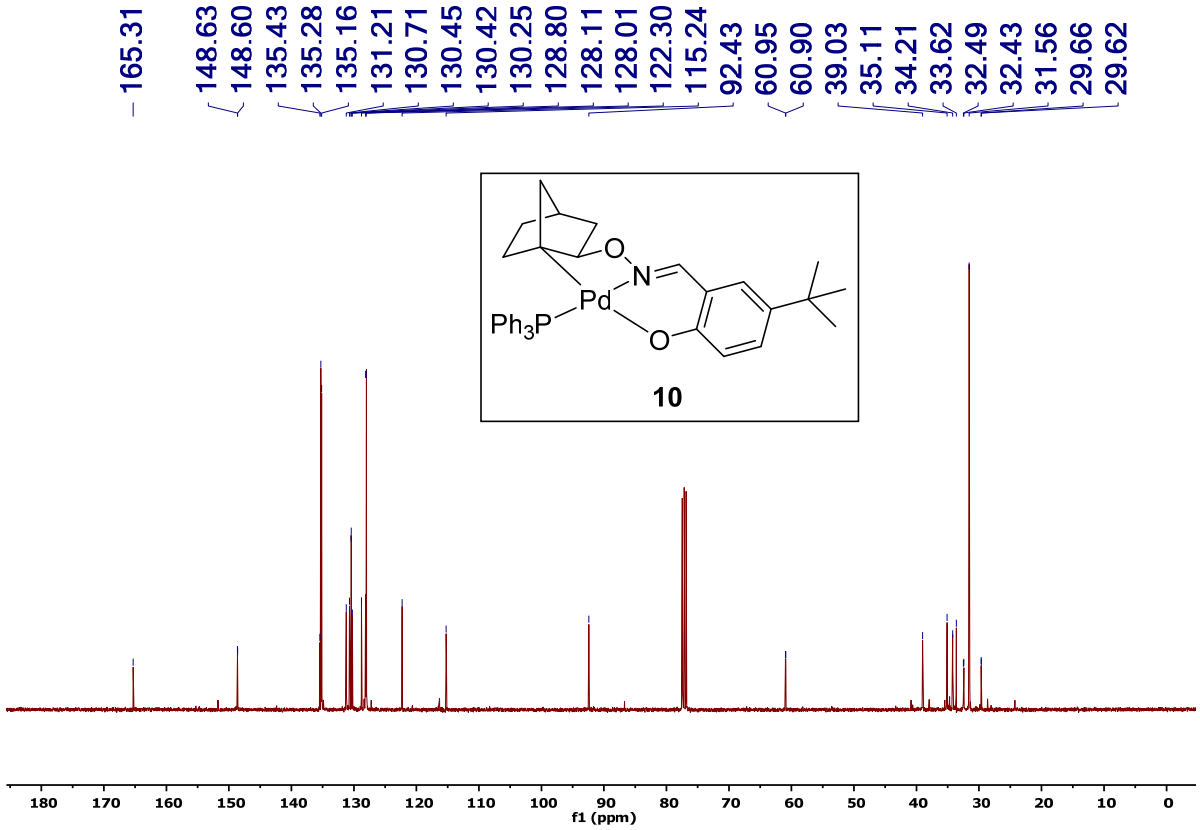
O
N
Pd
Ph3P
O
10
0.99 6.03 9.00 1.01 1.02 1.00 1.02 1.10 0.93 1.12 1.08 9.00 2.01 1.20 1.18 1.09
f1 (ppm)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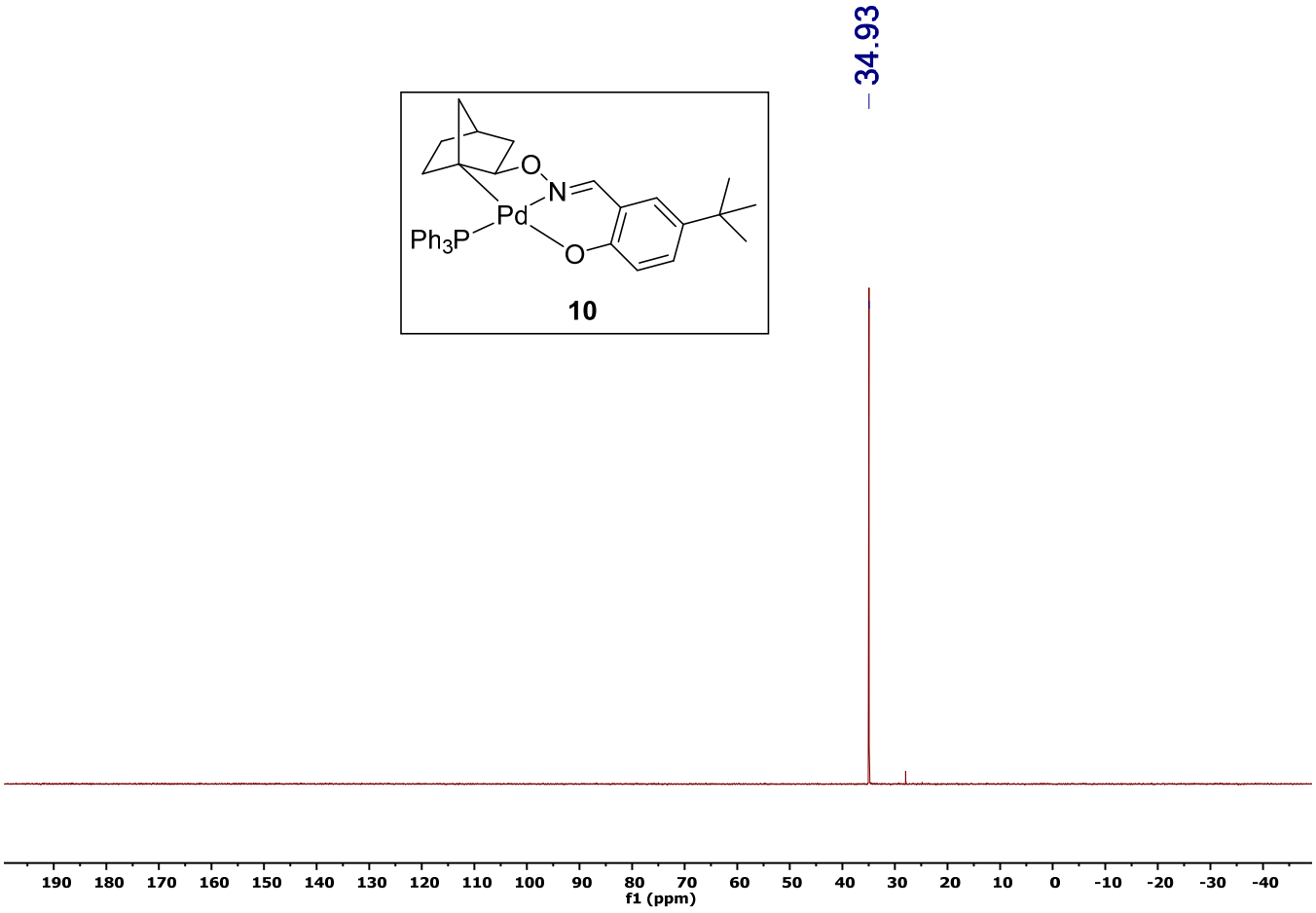
O
N
Pd
Ph3P
O
10
f1 (ppm)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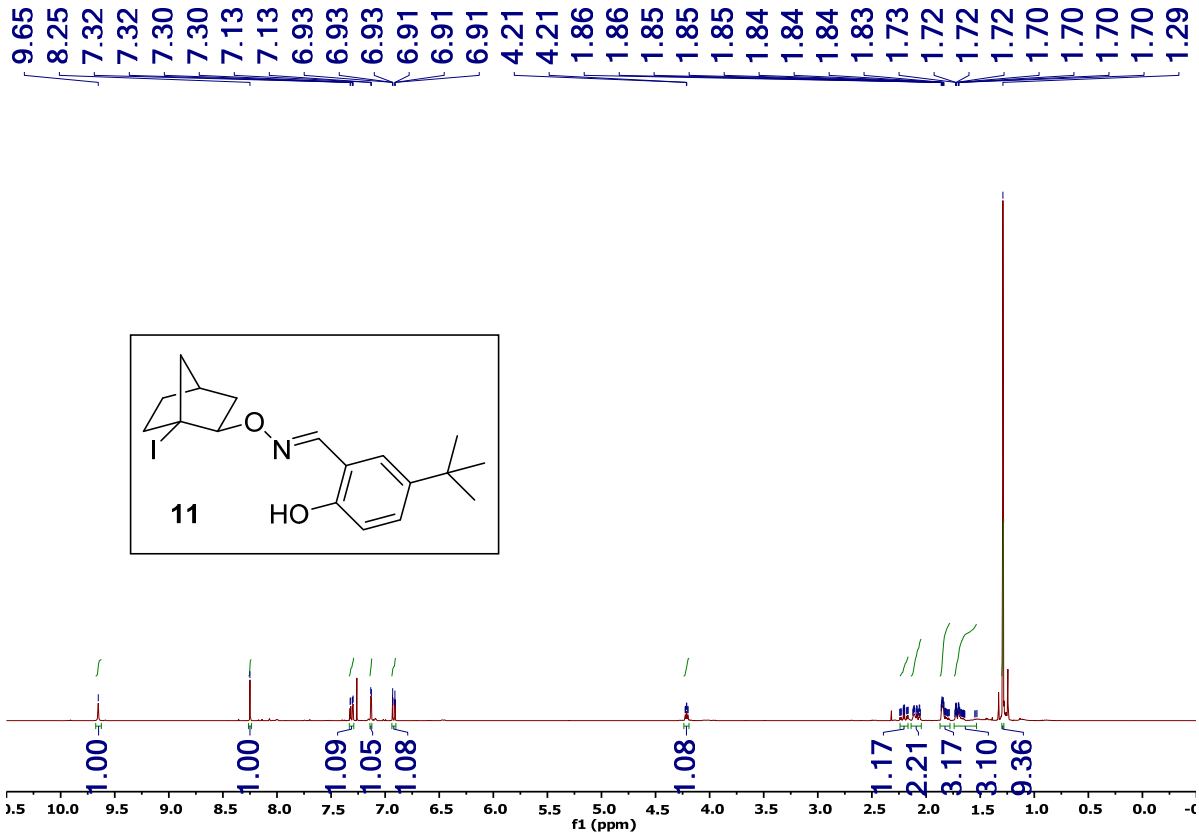
N
Pd
Ph3P
O
10
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)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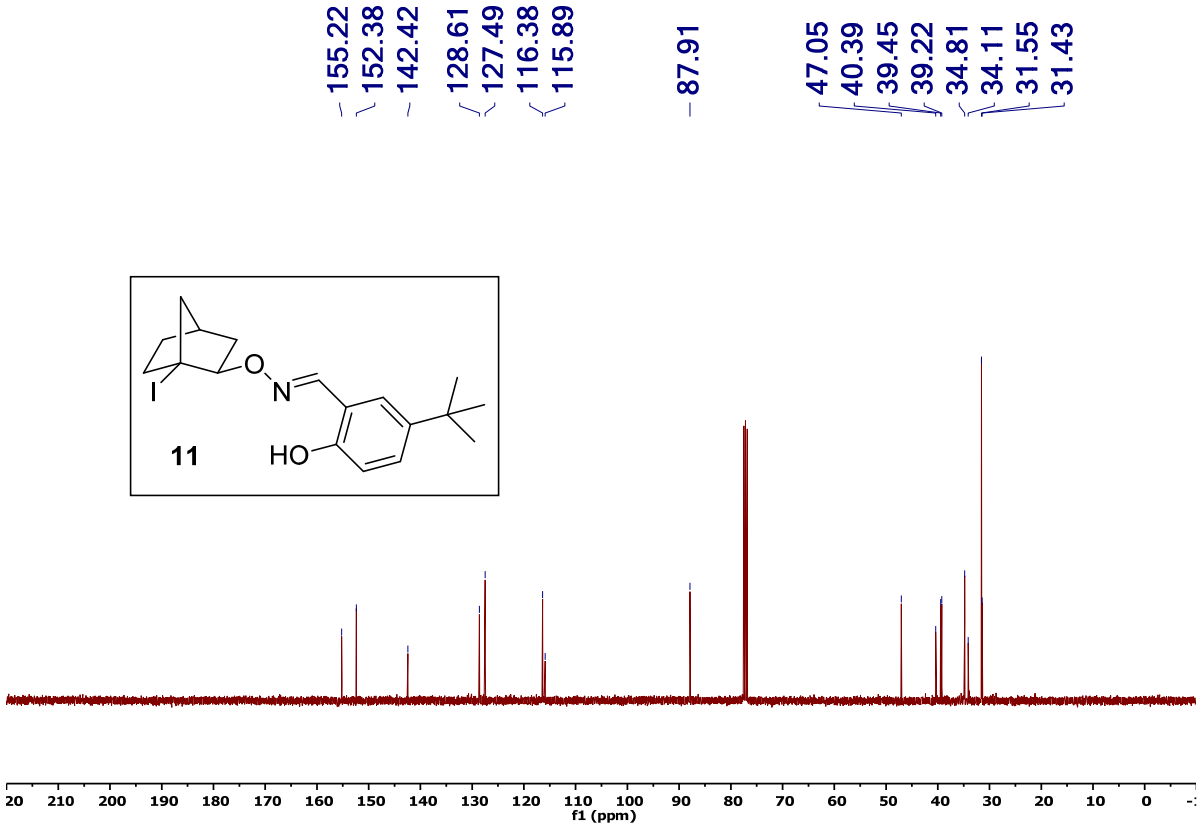
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40.39
39.45
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34.11
31.55
31.43
11
HO
f1 (ppm)