Supporting information for

[Pd(NHC)(PR_3)] (NHC = *N*-Heterocyclic Carbene) Catalyzed Alcohol Oxidation Using Molecular Oxygen

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General considerations

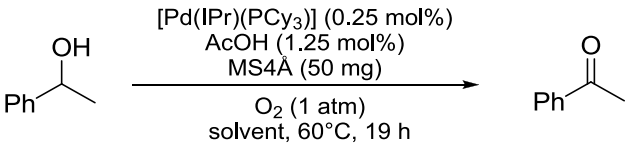
Unless otherwise stated, all reactions were performed under argon using standard Schlenk and glovebox techniques. Solvents were distilled from appropriate drying agents or were dispensed from a solvent purification system (SPS), other anhydrous solvents were purchased from Aldrich and degassed prior to use by. ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ Nuclear Magnetic Resonance (NMR) spectra were recorded on Bruker Avance 400 and 500 Ultrashield NMR spectrometers. Gas chromatography (GC) analyses were performed on an Agilent 7890A apparatus equipped with a flame ionization detector and a (5%-Phenyl)-methylpolysiloxane column (30 m, 320 µm, film: 0.25 µm). GC-conversions are based on comparison of signals of starting material and product. Signals of products were assigned based on comparison with commercially available authentic samples.

Catalysis

General procedure for the oxidation reaction

A Schlenk flask was charged with [Pd(IPr)(PCy_3)] (**1a**) (3.9 mg, 0.005 mmol), 4 Å molecular sieves (50 mg) and the substrate (if solid, 1 mmol). The inert atmosphere was exchanged for oxygen by 3 evacuation-backfill cycles. Solvent (2 mL) and AcOH (1.5 µL, 0.025 mmol) were then added, followed by the substrate (if liquid, 1 mmol). The reaction mixture was stirred at 60°C and monitored by GC. The reaction mixture was then purified by flash column chromatography (SiO_2, pentane).

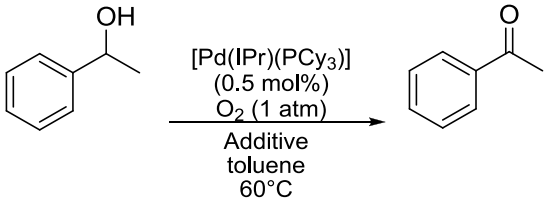
Table S1: ***Solvent screening***[a]



Entry	Solvent	Conversion [%][b]
1	DMSO	28
2	DMF	16
3	MeCN	12
4	THF	34
5	Toluene	74

[a]Reaction conditions: Phenylethanol (121 µL, 1.00 mmol), MS4Å (50 mg), toluene (2 mL) O_2 (1 atm) [b]Conversions determined by GC.

Table S2: ***Effect of additives***[a]



Entry	Additive	Desiccant	Time [h]	Conversion [%][b]
1	HOAc (5 mol%)	4Å-MS (50mg)	21	73
2	Tartaric acid (5 mol%)	4Å-MS (50mg)	21	1
3	HOAc (10 mol%)	4Å-MS (50mg)	16	8
4	HOAc (5 mol%)	4Å-MS (50mg)	16	30
5	HOAc (2.5 mol%)	4Å-MS (50mg)	16	96
6	HOAc (1 mol%)	4Å-MS (50mg)	20	83
7	TFA (2.5 mol%)	4Å-MS (50mg)	16	22
8	HOAc (2.5 mol%)	Na_2SO_4 (50mg)	66	15
9	HOAc (2.5 mol%)	$MgSO_4$ (50mg)	66	12
10	HOAc (2.5 mol%)	K_2CO_3 (50mg)	66	17

[a]Reaction conditions: Phenylethanol (121 µL, 1.00 mmol), Additive (50 mg), toluene (2 mL) O_2 (1 atm) [b]Conversions determined by GC.

NMR data of oxidation products

4-methoxy-acetophenone[1]

^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) = 7.84–7.79 (m, 2 H), 6.84–6.74 (m, 2 H), 3.74 (s, 3 H), 2.42 (s, 3 H).

2-methyl-acetophenone[2]

^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) = 7.62–7.56 (m, 1 H), 7.31–7.24 (m, 1 H), 7.20-7.10 (m, 2 H), 3.48 (s, 3 H), 2.44 (s, 3 H).

4-methyl-acetophenone[3]

^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) = 7.75 (d, ^3J= 7.9 Hz, 2 H), 7.14 (d, ^3J = 7.9 Hz, 2 H), 2.46 (s, 3 H), 2.29 (s, 3 H).

4-trifluoromethyl-acetophenone[4]

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.98 (d, ^{3}J= 8.7 Hz, 2 H), 7.64 (d, ^{3}J= 8.7 Hz, 2 H),.2.56 (s, 3 H).

Propiophenone[5]

^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) = 8.01-7.94 (m, 2 H), 7.59-7.52 (m, 1 H),.7.50-7.42 (m, 2 H), 3.00 (q, ^{3}J= 7.2 Hz, 2 H), 1.24 (t, ^{3}J= 7.0 Hz, 3 H).

Benzophenone[6]

^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) = 7.73–7.65 (m, 4 H), 7.51–7.42 (m, 2 H), 7.40-7.31 (m, 4 H).

α-Tetralone[7]

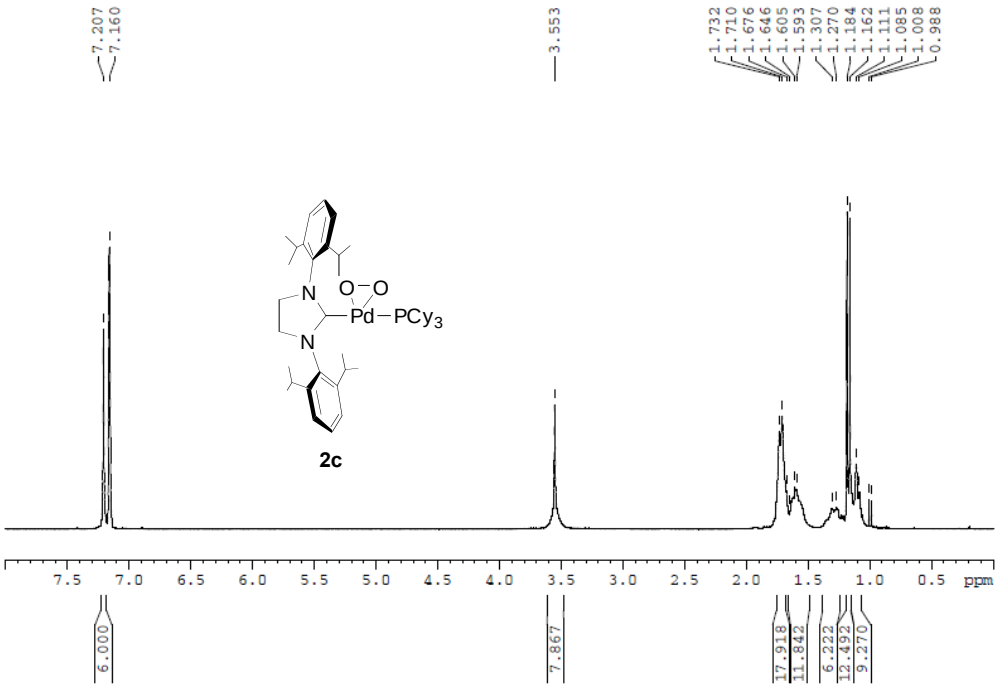
^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) = 7.92 (dd, ^{3}J = 7.2 Hz. ^{3}J = 1 Hz, 2 H), 7.37 (dt, ^{3}J = 7.5 Hz, ^{3}J = 1.5 Hz), 7.23-7.10 (m, 2 H), 2.85 (t, ^{3}J= 6.2 Hz, 2 H), 2.54 (t, ^{3}J= 7.0 Hz, 2 H), 2.02 (q, ^{3}J= 5.6 Hz, 2 H).

Camphor[8]

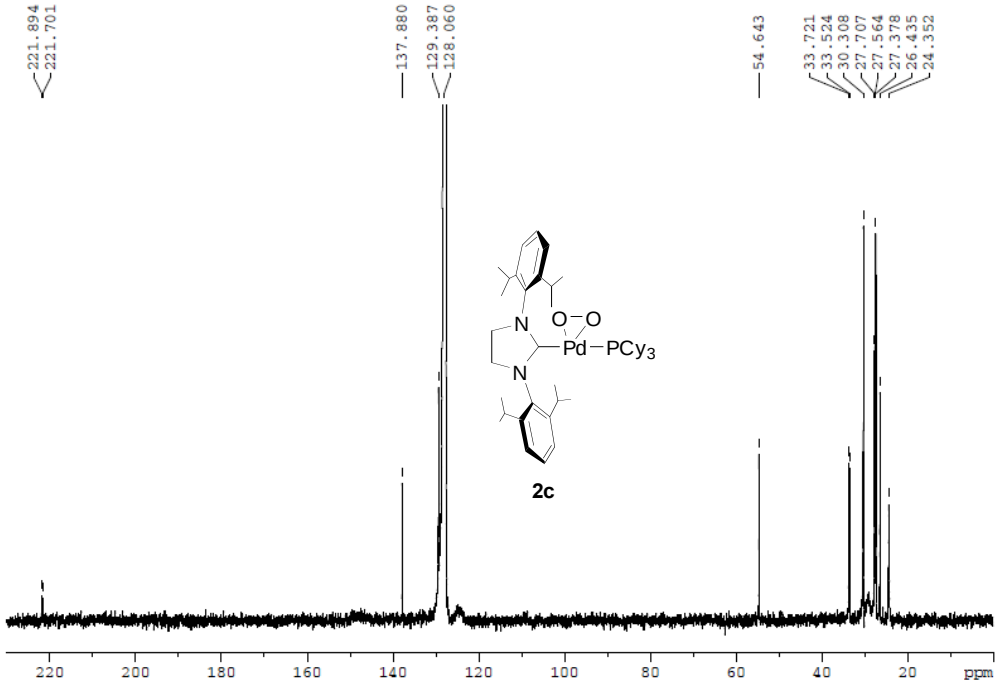
^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 2.32-2.24 (m, 1 H), 2.02 (t, ^{3}J= 4.64, 1 H), 1.93-1.83 (m, 1 H), 1.77 (d, ^{3}J= 18 Hz, 1 H), 1.66-1.57 (m, 1 H), 7.37 (dt, ^{3}J= 7.5 Hz, ^{3}J= 1.5 Hz), 1.37-1.22 (m, 2 H), 0.89 (s, 3 H), 0.84 (s, 3 H) 0.77 (s, 3 H).

NMR spectra of complexes

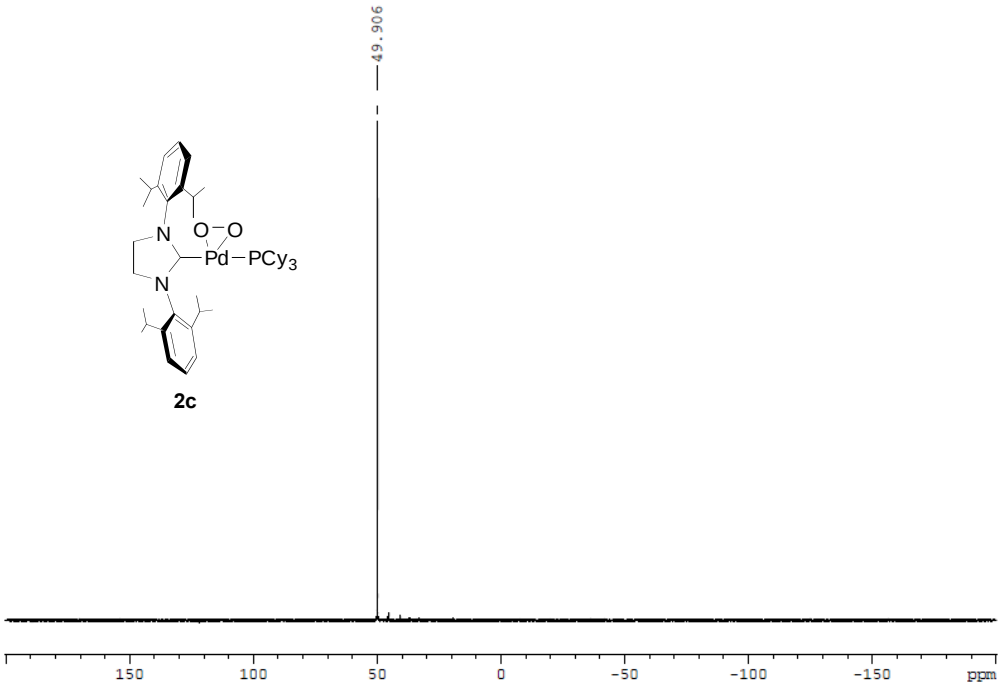
^{1}H of $[Pd(\eta^2\text{-}O_2)(SIPr)(PCy_3)]$ in C_6D_6 (2c)



$^{13}C\{^{1}H\}$ of $[Pd(\eta^2\text{-}O_2)(SIPr)(PCy_3)]$ in C_6D_6 (2c)

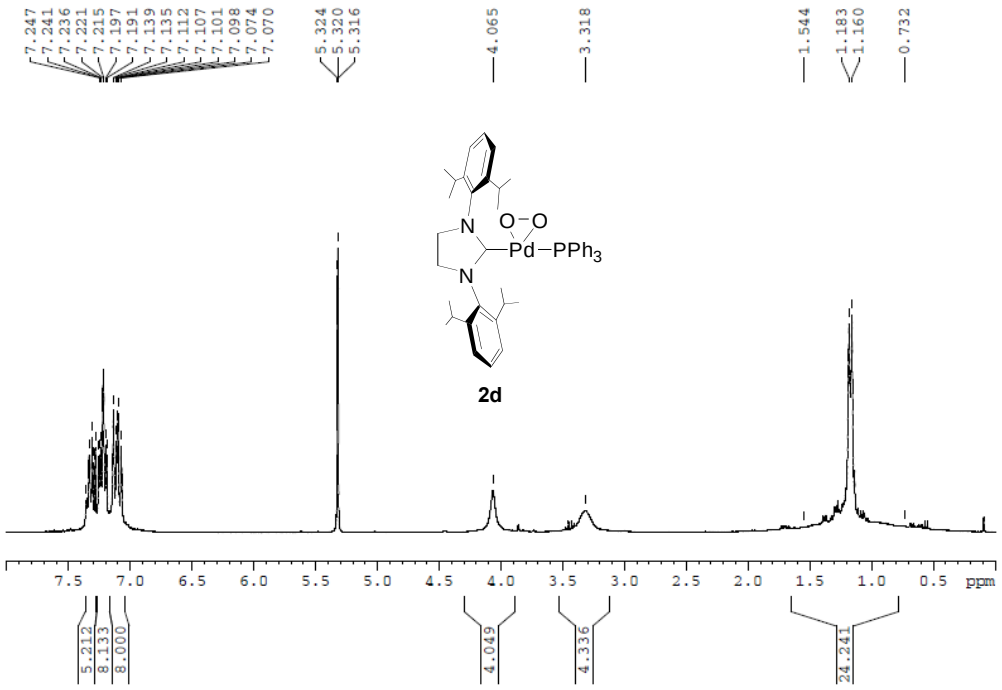


$^{31}P\{^{1}H\}$ of $[Pd(\eta^2\text{-}O_2)(SIPr)(PCy_3)]$ in C_6D_6 (2c)



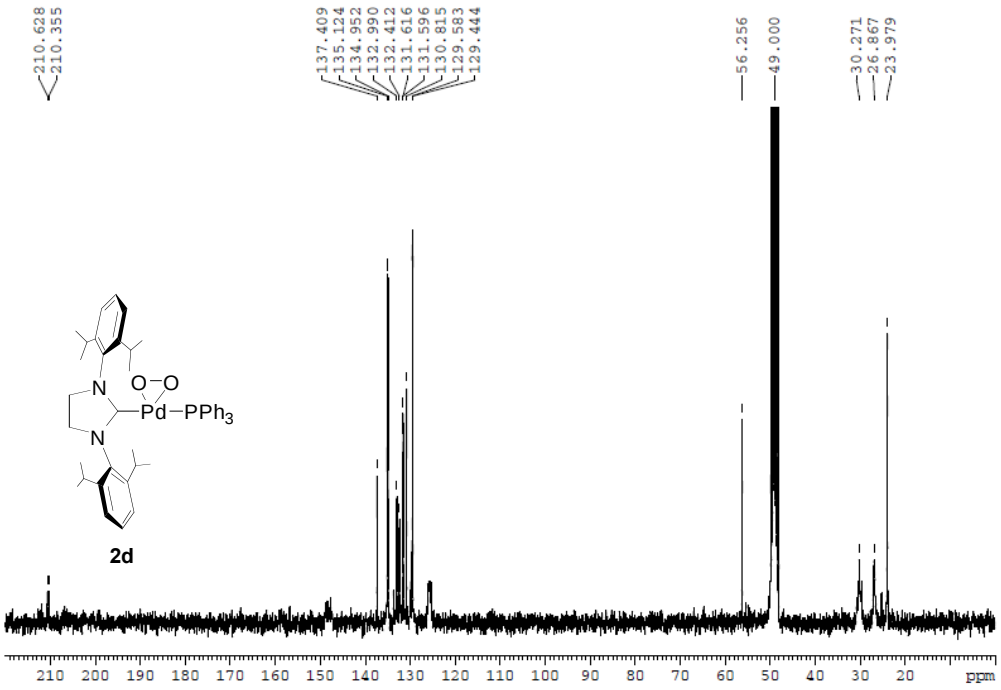
2c

^{1}H $[Pd(\eta^2\text{-}O_2)(SIPr)(PPh_3)]$ in CD_2Cl_2 (2d)

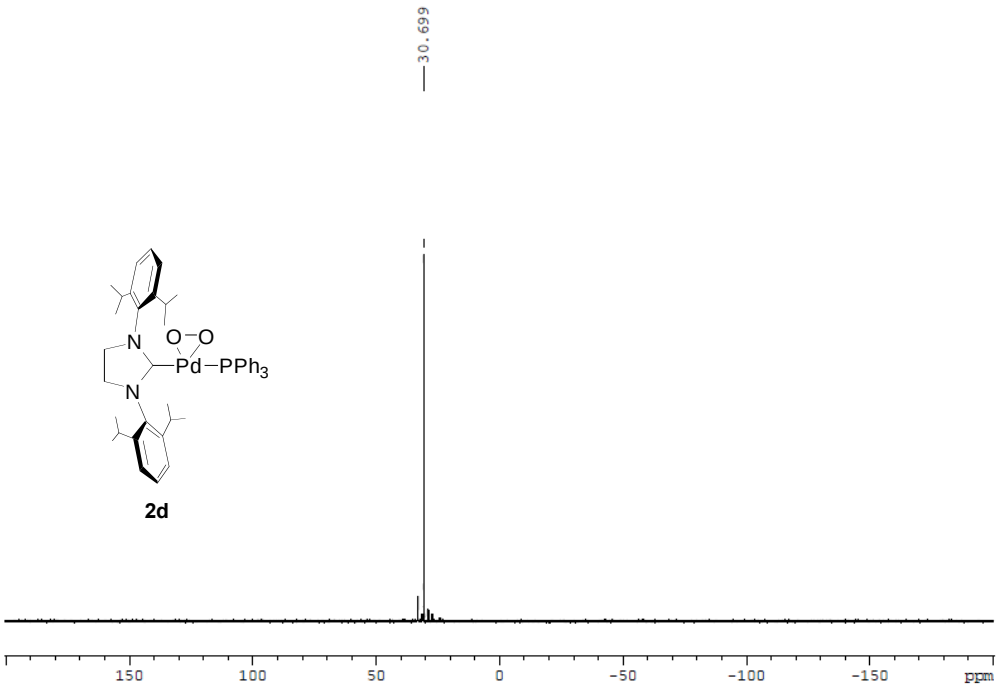


2d

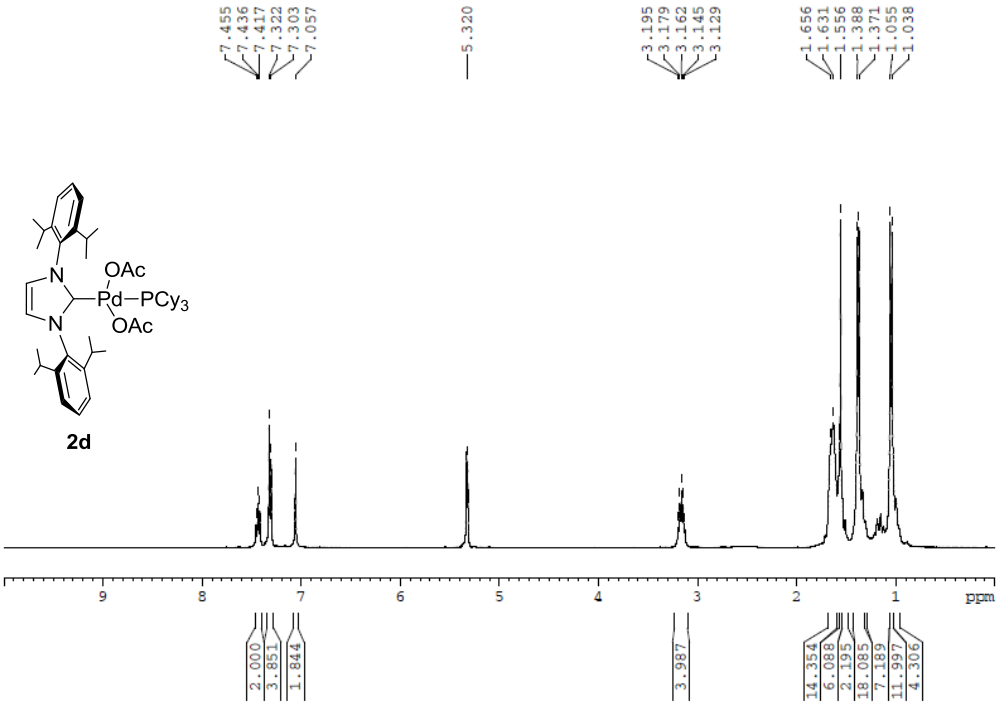
$^{13}C\{^{1}H\}$ of $[Pd(\eta^2\text{-}O_2)(SIPr)(PPh_3)]$ in CD_3OD(2d)



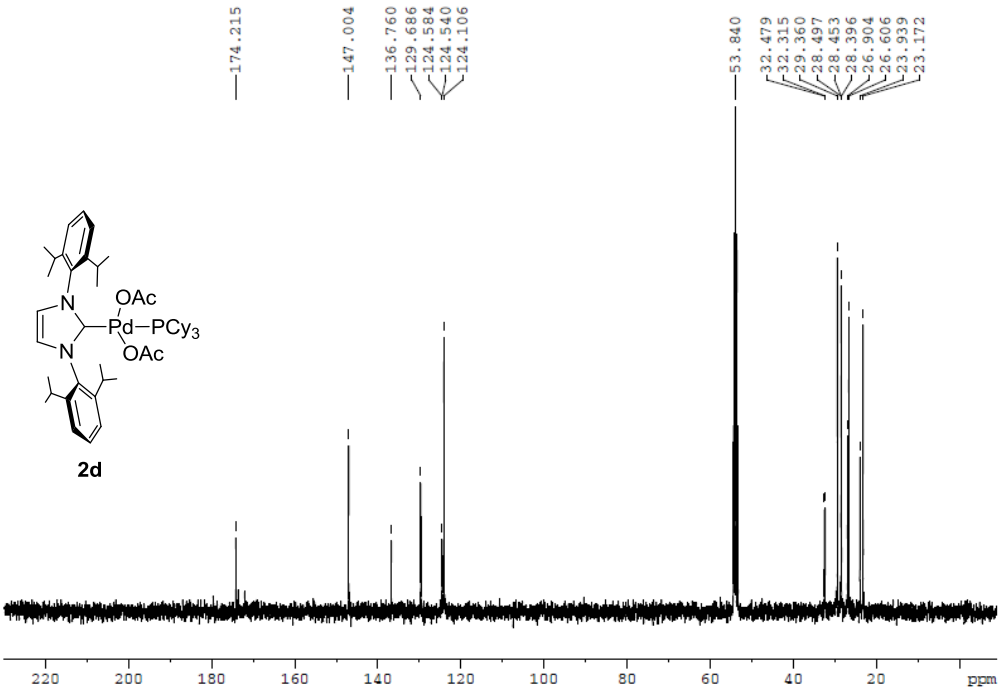
$^{31}P\{^{1}H\}$ of $[Pd(\eta^2\text{-}O_2)(SIPr)(PPh_3)]$ in CD_2Cl_2 (2d)



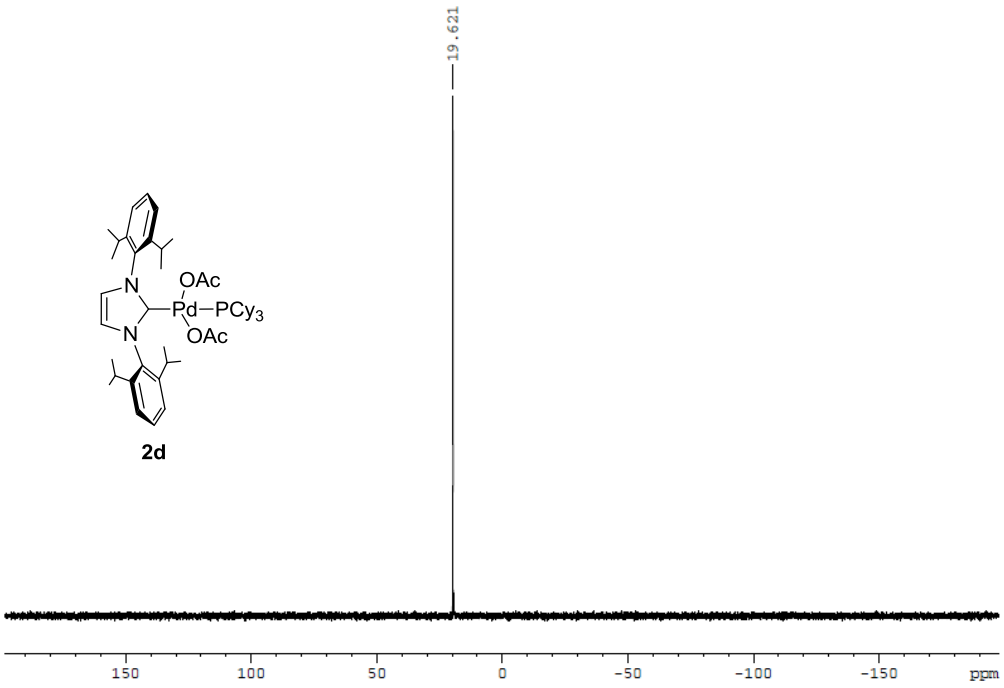
^{1}H of $[Pd(OAc)_2(IPr)(PCy_3)]$ in CD_2Cl_2 (3)



$^{13}C\{^{1}H\}$ of $[Pd(OAc)_2(IPr)(PCy_3)]$ in CD_2Cl_2 (3)

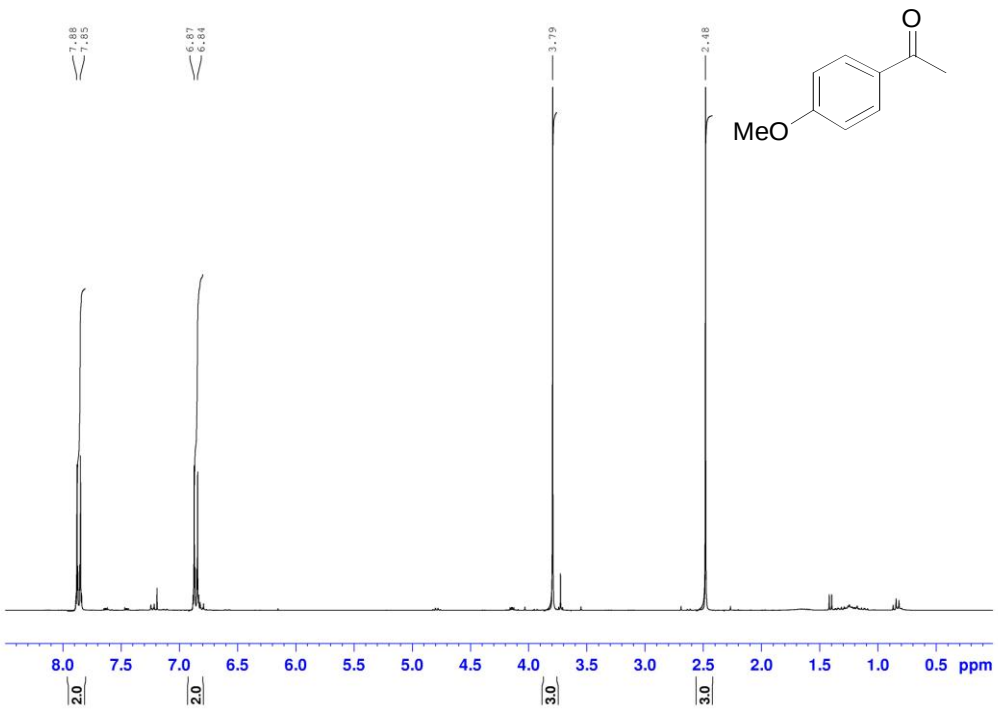


$^{31}P\{^{1}H\}$ of $[Pd(OAc)_2(IPr)(PCy_3)]$ in CD_2Cl_2 (3)

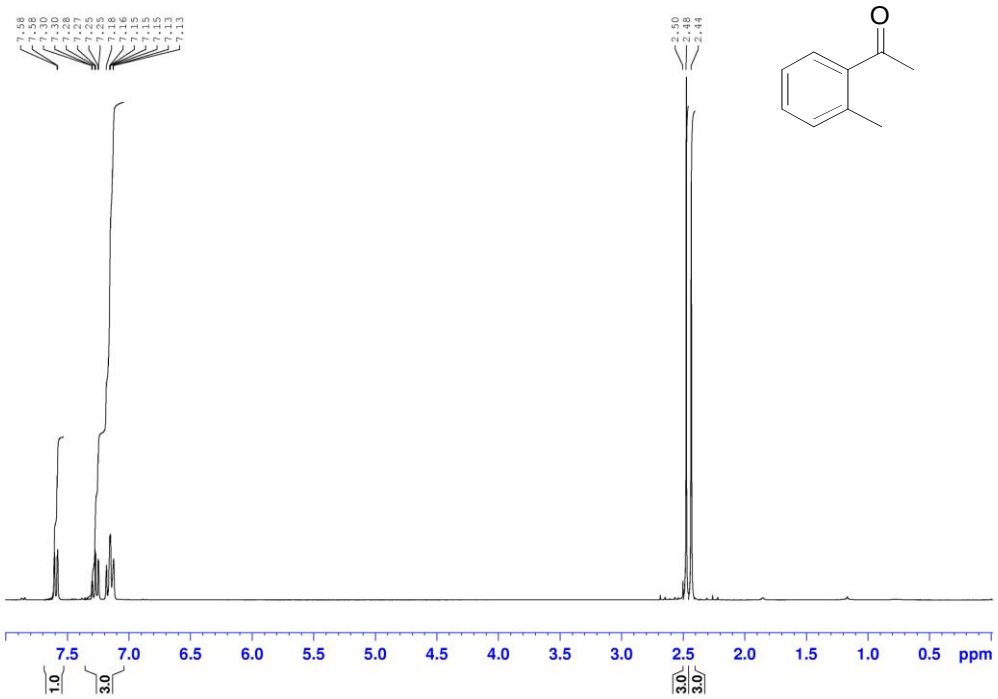


NMR spectra of catalysis products

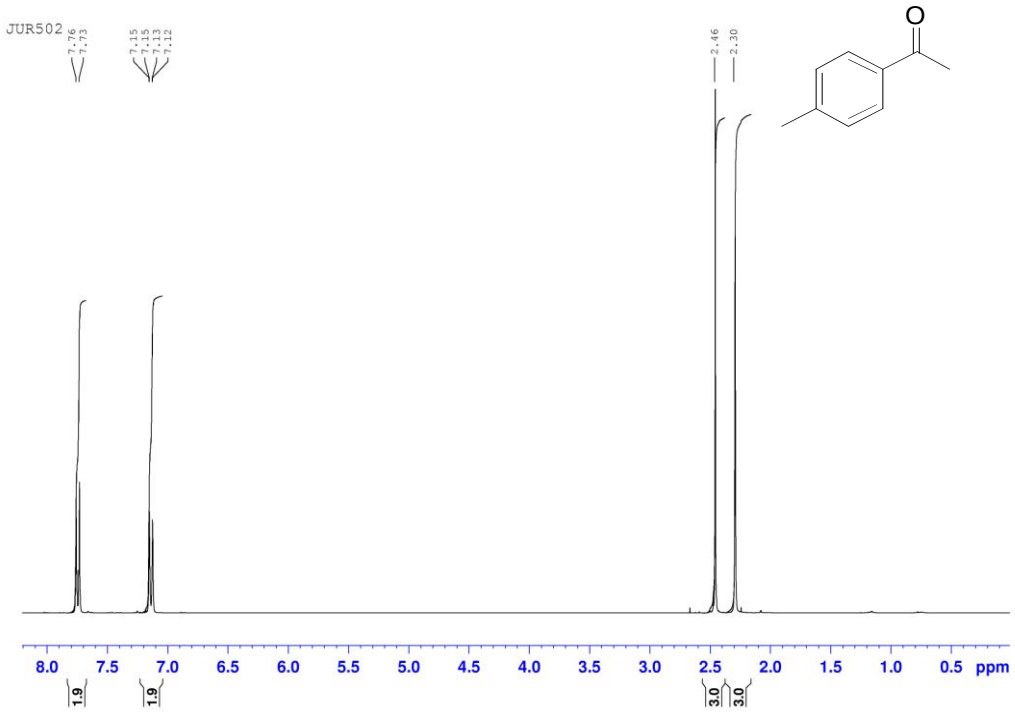
4-methoxy-acetophenone



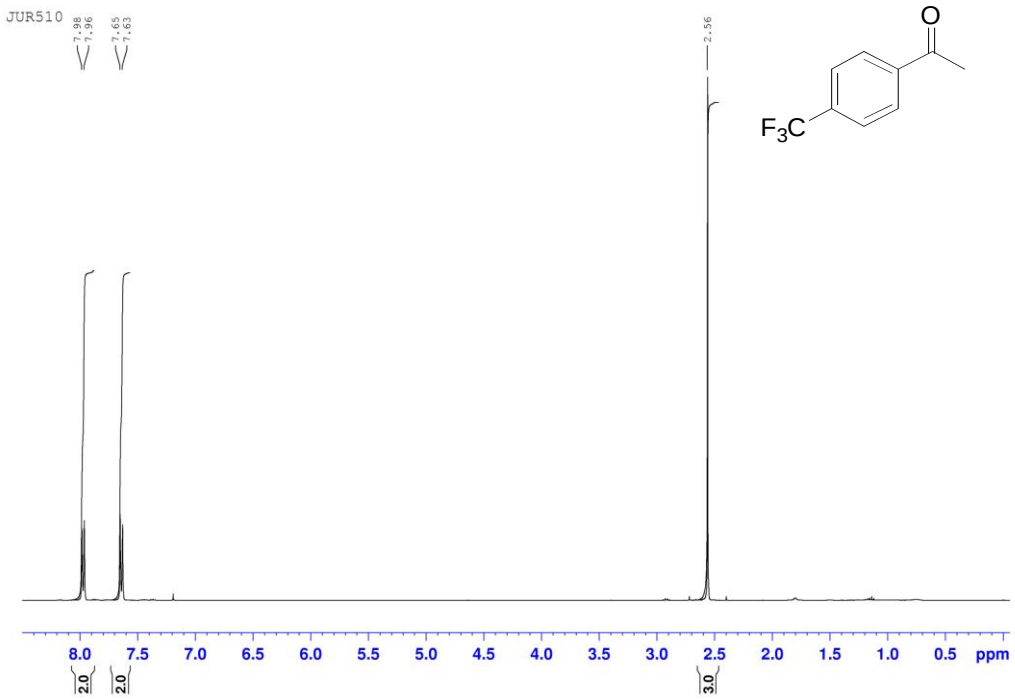
2-methyl-acetophenone



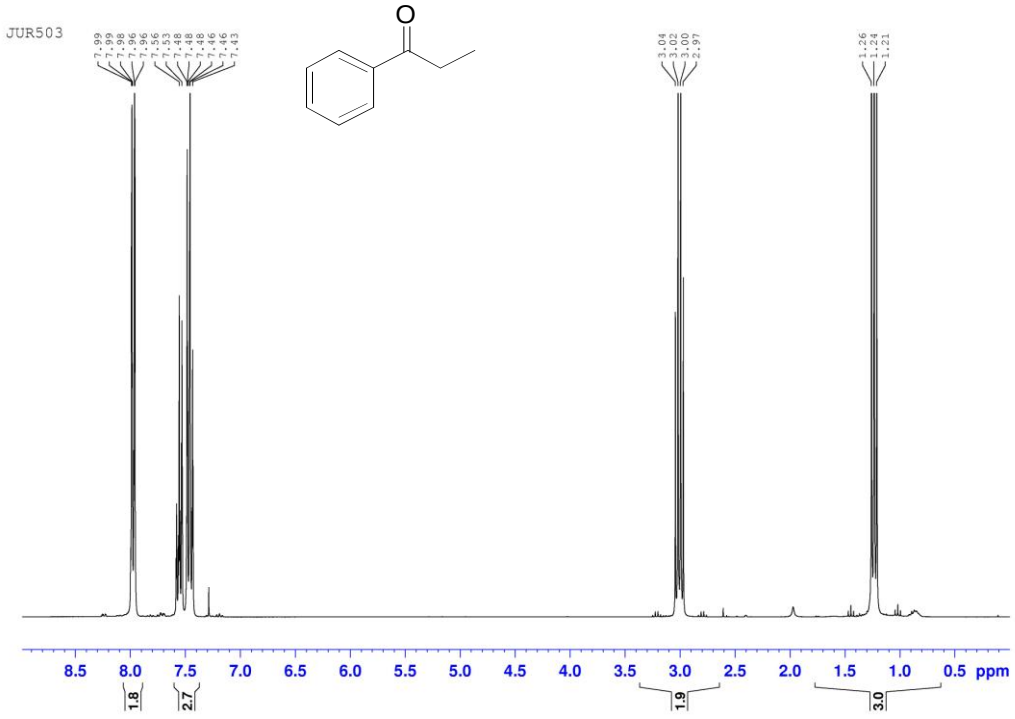
4-methyl-acetophenone



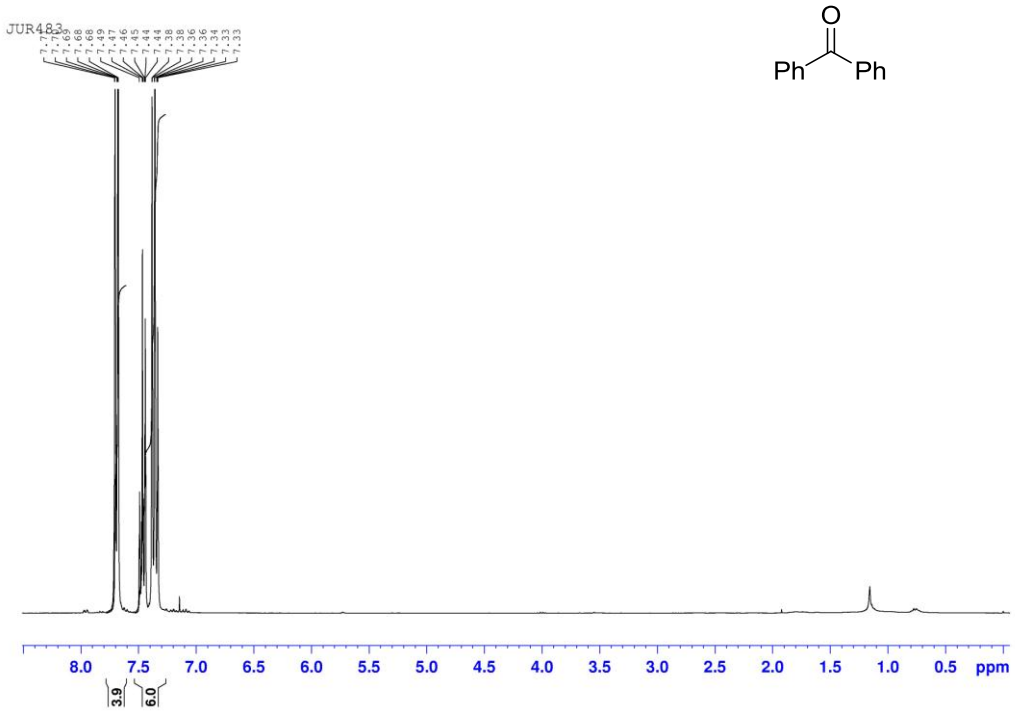
4-trifluoromethyl-acetophenone



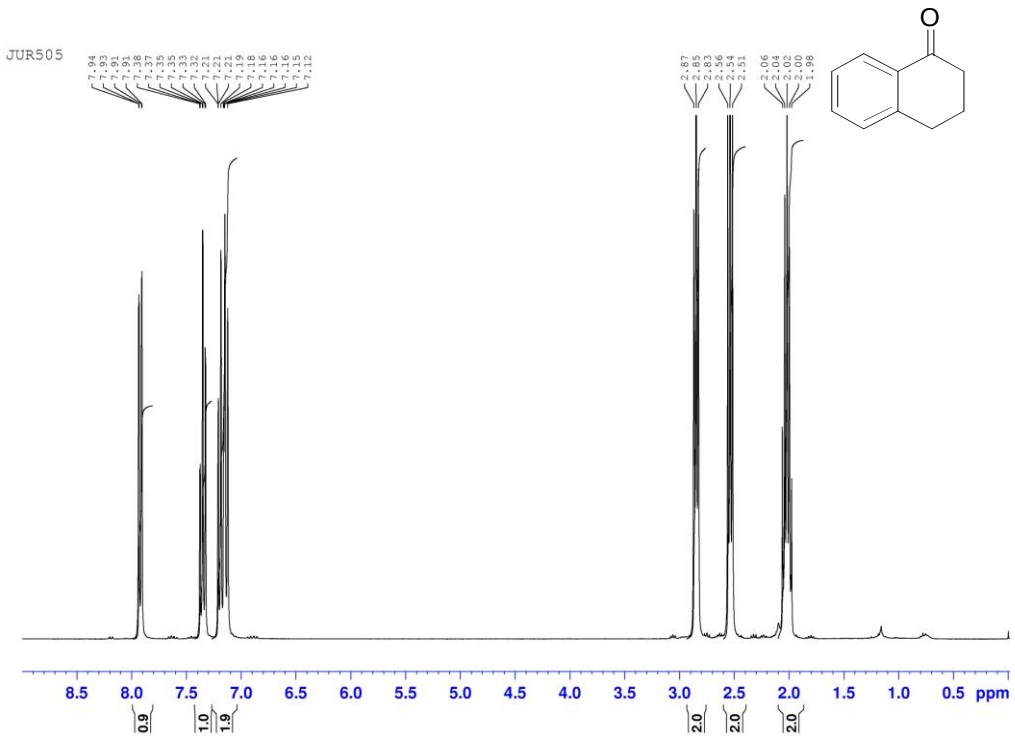
Propiophenone



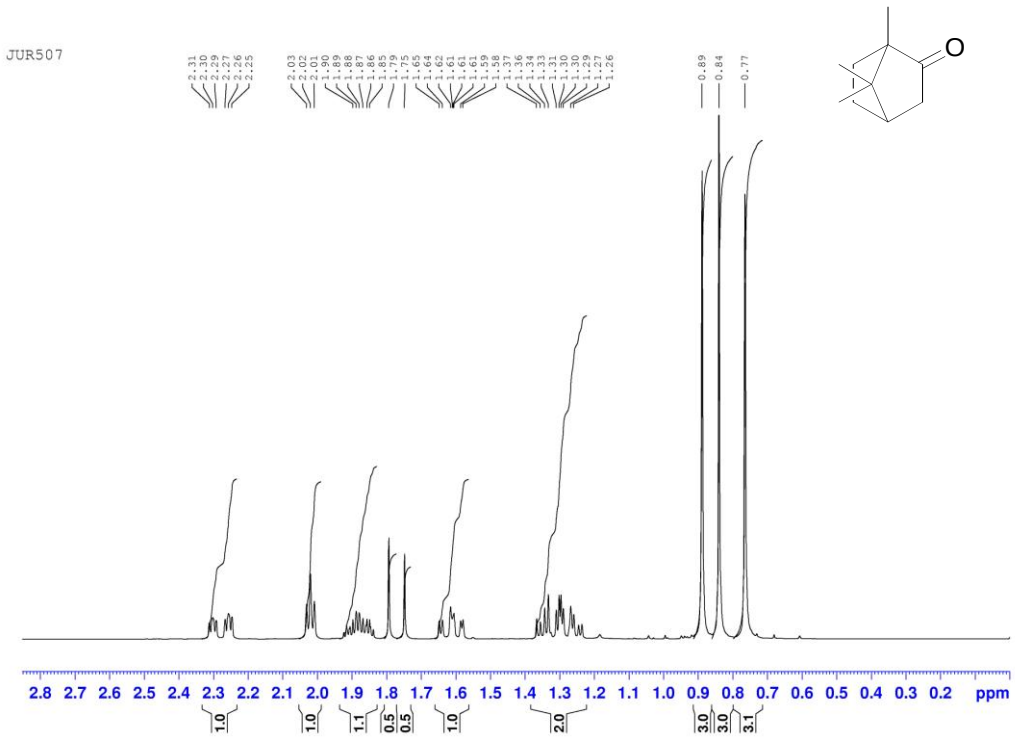
Benzophenone



α-Tetralone

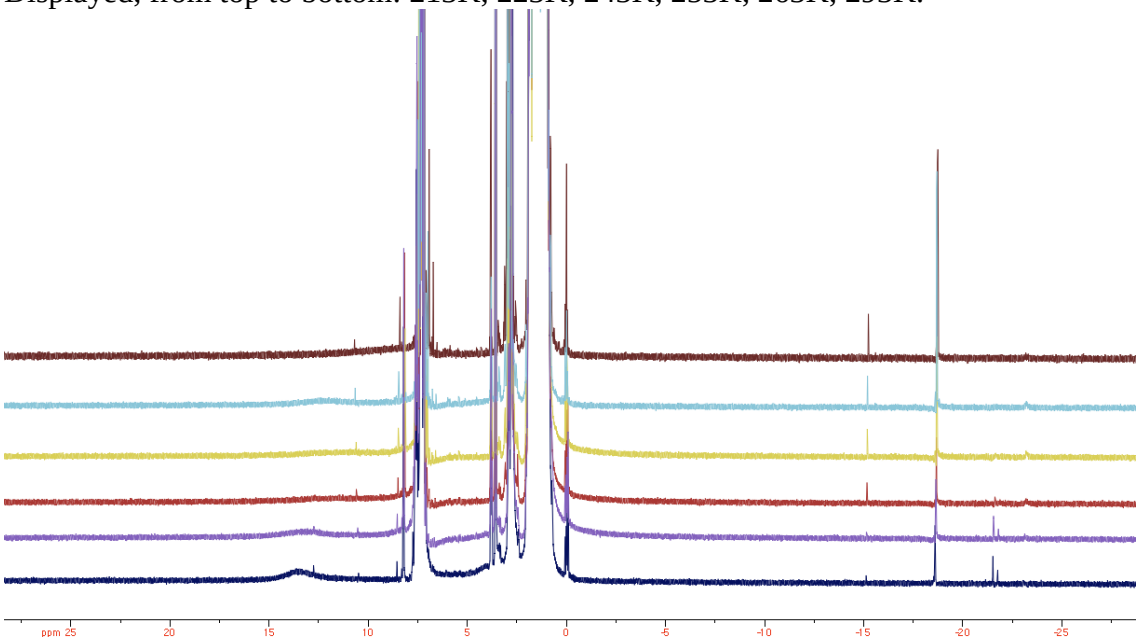


Camphor

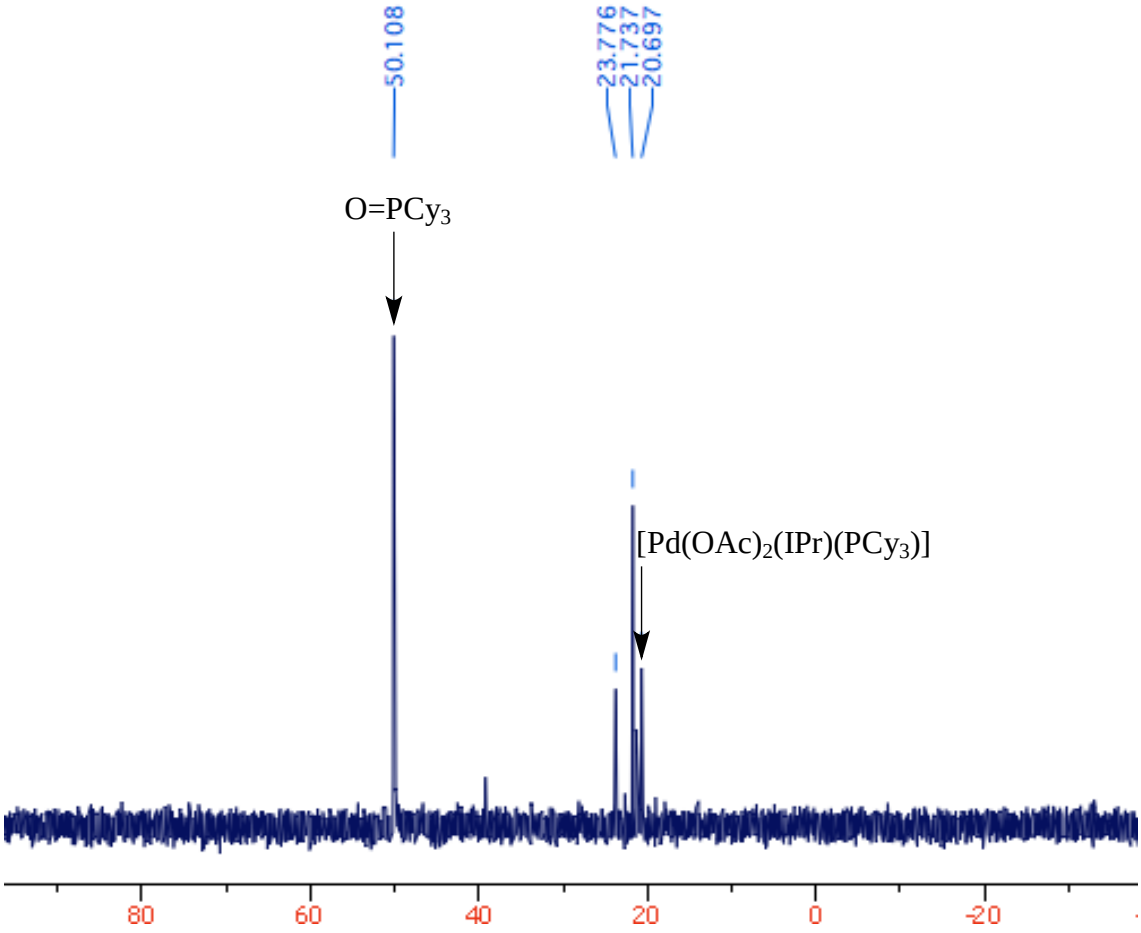


NMR spectra for mechanistic investigations

^{1}H NMR Spectra for the reaction of [Pd(IPr)(PCy_3)],with 1 eq. of acetic acid, in THF-d^4 Displayed, from top to bottom: 213K, 223K, 243K, 253K, 263K, 293K.



^{31}P{^{1}H} NMR Spectra for the reaction of [Pd(IPr)(PCy_3)] with O_2 in C_6D_6 followed by the addition of 2 eq. of acetic acid.



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[4] C. J. Pouchert, J. Behnke, *The Aldrich Library of ^{13}C and ^{1}H FT NMR Spectra, 1. Ed.*, **vol 2**, 831A, CAS [709-63-7] and references cited.
[5] C. J. Pouchert, J. Behnke, *The Aldrich Library of ^{13}C and ^{1}H FT NMR Spectra, 1. Ed.*, **vol 2**, 802B, CAS [93-55-0] and references cited.
[6] C. J. Pouchert, J. Behnke, *The Aldrich Library of ^{13}C and ^{1}H FT NMR Spectra, 1. Ed.*, **vol 2**, 884C, CAS [119-61-9] and references cited.
[7] C. J. Pouchert, J. Behnke, *The Aldrich Library of ^{13}C and ^{1}H FT NMR Spectra, 1. Ed.*, **vol 2**, 810C, CAS [529-34-0] and references cited.
[8] C. J. Pouchert, J. Behnke, *The Aldrich Library of ^{13}C and ^{1}H FT NMR Spectra, 1. Ed.*, **vol 1**, 678C, CAS [76-22-2] and references cited.