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Palladium Catalyzed Oxidative Carbonylation of Alcohols: Effects of the Diphosphine Ligands

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SUPPORTING INFORMATION

1. Table 1S

Table 1S. Bite angle-effect on the oxidative carbonylation reaction

Entry	P∩P	β_n [º]	TOF [mol/(mol·h)]			Selectivity [%]		
			O	**C**	**A**	**O**	**C**	**A**
1	dppe	78.1	0.6	0.5	1.3	25	20	55
2	dppp	86.2	4.0	2.0	5.9	33	17	50
3	dppb	98.7	116	29	41	62	16	22
4	dppf	99.1	245	6	15	92	2	6
5	DPEphos	102.9	39	14	8	64	23	13
6	Xantphos	110.0	3.0	4.1	1.8	34	46	20
7	SPANphos	171.9[b]	1.1	1.9	0.9	29	49	22

Conditions: $[Pd(OH_2)_n(OTs)_{2-n}(P\cap P)](TsO)_n$ (n = 0, 1)] = 2.10^{-4} mol/L, Pd/BQ/NEt_3 = 1/700/2, P_{CO} = 80 atm, T = 80 °C, 1 h, 5 mL anhydrous *i*PrOH.

2. Figure 1S

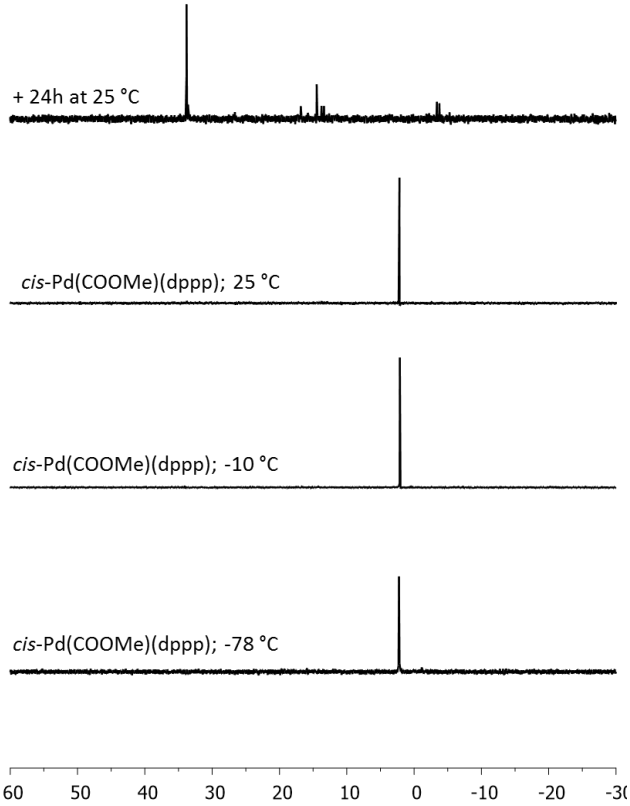
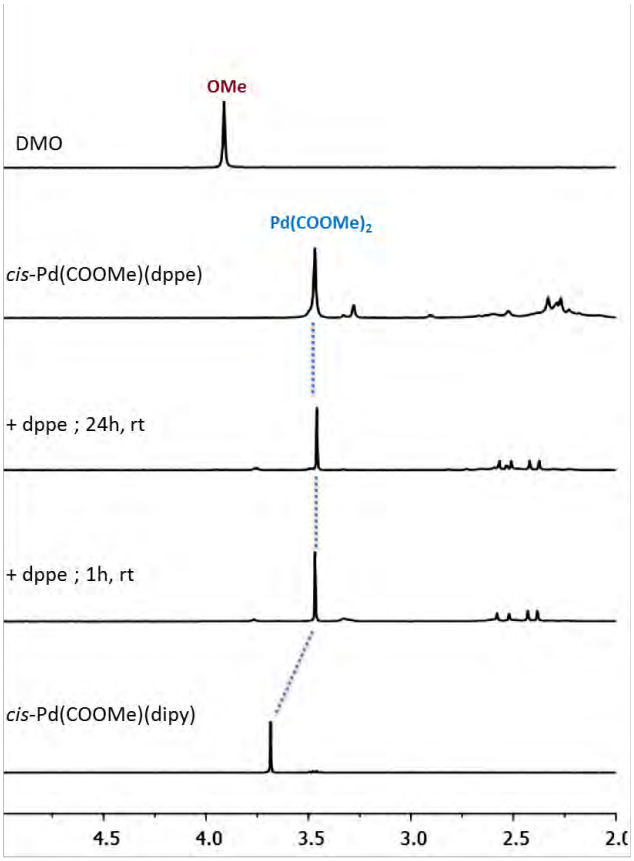


Figure 1S. $^{31}P\{^{1}H\}$ NMR spectra relevant to the stability of *cis*–[$Pd(COOMe)_2(dppp)$] in $CDCl_2$.

3. Figure 2S



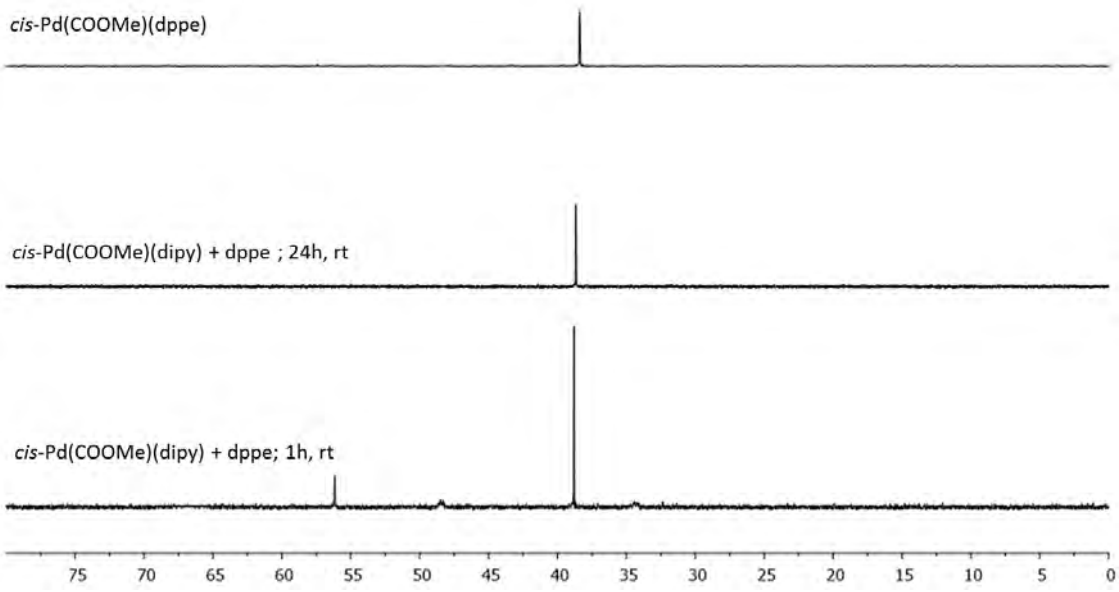


Figure 2S. ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra relevant to the reaction between the *cis*–[$Pd(COOMe)_2$(dipy)] (0.01 mmol) and dppe (0.01 mmol) in 1 mL of $CDCl_2$.

4. Figure 3S

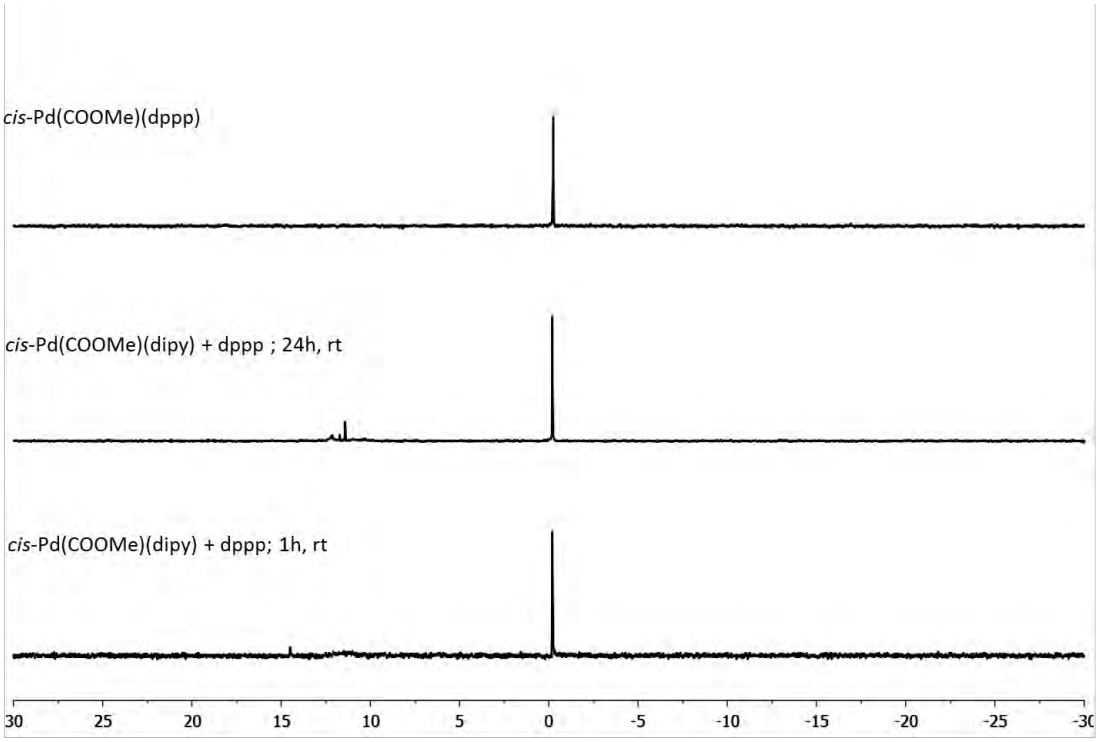


Figure 3S. $^{31}P\{^{1}H\}$ NMR spectra relevant to the reaction between the *cis*–[$Pd(COOMe)_2$(dipy)] (0.01 mmol) and dppp (0.01 mmol) in 1 mL of $CDCl_2$.

2. Experimental

2.1 General Procedures

All reactions were carried out using standard Schlenk techniques under argon atmosphere. Chemicals were purchased from Sigma–Aldrich, Acros Chimica, Strem Chemicals and Eurisotop. NMR spectra were recorded on Bruker 400 and 500 MHz spectrometers. ^{31}P and ^{13}C spectra were measured ^{1}H decoupled. All ^{1}H and ^{13}C chemical shifts are reported relative to the residual proton resonance in the deuterated solvents. $^{31}P\{^{1}H\}$ signals were referenced to an 85 % aqueous solution of H_3PO_4. NMR under pressure was performed using a 5 mm sapphire HP–NMR tube with titanium head. Infrared spectra were recorded on a Nicolet FT–IR spectrophotometer. Mass spectra were run by MALDI–TOF on a Bruker Daltonics Autoflex spectrometer. GC analysis was performed on: a) Hewlett–Packard Model 6890 chromatograph fitted with HP5, 30 m × 0.32 μm × 0.25 μm column (detector: FID; carrier gas: N_2, 0.7 mL/min; oven: 40 °C (3.5 min) to 250 °C at 15 °C/min). b) Hewlett–Packard Model 5890 Series II chromatograph fitted with 20 % Carbowax 20 M on 80–100 mesh Chromosob W, 1 m × 2.3 mm ID packed column (detector: FID; carrier gas: N_2; 25 mL/min; oven: 80°C). Carbon monoxide (purity 99.9 %) was supplied by Carburos Metálicos. The dppe, dppp, dppb, dppf, dippf, dtbpf, dcypf, Xantphos, DPEphos, (pOCH$_3$–C$_6$H$_4$)$_2$PCl , (pCF$_3$–C$_6$H$_4$)$_2$PCl, $PdCl_2$, $Pd(OAc)_2$, Ag(OTs), TsO·H_2O, NEt_3, TMDA, n–BuLi, Na_2SO_4, and anhydrous solvent (acetone, THF, CH_2Cl_2, n–hexane and Et_2O) were purchased from commercial sources and used as received. 1,4–benzoquinone (BQ) was purified before use from ethyl ether. Dry iPrOH and MeOH were obtained by distillation over Mg and I_2 and stored over 4Å molecular sieves under argon. Dry $CDCl_3$ and CD_2Cl_2 were distilled over P_2O_5 and stored over 4Å molecular sieves under Ar. pOMe–dppf,[1] SPANphos,[2] *cis*–[Pd(OAc)$_2$(dppp)] and *cis*–[Pd(OH$_2$)(OTs)(dppp)](TsO),[3] *cis*-[Pd(OAc)$_2$(dppb)],[4] [PdCl$_2$(CH$_3$CN)$_2$],[5] *cis*–[PdCl$_2$(dppf)],[6] and *cis*–[Pd(COOMe)$_2$(dipy)][7] were prepared according to literature procedures.

2.2 Synthesis of pCF$_3$–dppf

This ligand was synthesized and manipulated under an argon atmosphere. To a solution of ferrocene (0.24 g, 1.3 mmol) in n–hexane (7 mL) n–BuLi (0.18 g, 2.8 mmol) and TMDA (0.31 g, 2.7 mmol) were quickly added and the resulting mixture was stirred at 60 °C for 1h. The heating bath was removed, and 3 mL of dry THF were added. The dark brown suspension was cooled to –78 °C and a solution of (pCF$_3$–C$_6$H$_4$)$_2$PCl (1.00 g, 2.8 mmol) in THF (2 mL) was added within 10 min. The reaction mixture was allowed to warm overnight at room temperature. The solvent was removed *in vacuo*, Et_2O (20 mL) was added to the residual oil and the insoluble solid was removed by filtration. The filtrate was washed with water and the organic layer was dried over Na_2SO_4 and the solvent was removed *in vacuo*. pCF$_3$–dppf was purified by rotative chromatography on silica gel using n–hexane. The crude products were recrystallized from n–hexane. Yield: (215 mg) 20 %. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.58 (d, J = 7.70 Hz, 8 H), 7.38 (t, J = 7.70 Hz, 8 H), 4.34 (t, J= 1.81 Hz, 4H), 4.00 (q, J = 1.81 Hz, 4H). $^{31}P\{^{1}H\}$ NMR (161 MHz, $CDCl_3$, 25 °C): δ –13.65. ^{13}C

NMR (100 MHz, $CDCl_3$, 25 °C): 133.6 (d, J = 19.3 Hz), 125.0 (m), 77.21 (s), 77.8 (d, J = 14.5 Hz), 72.7 (m). MALDI–MS: 826.1 $[M]^+$.

2.3 Preparation of the complexes

All the operations were made in argon atmosphere by schlenk technique using anhydrous solvents.

2.3.1 Synthesis of cis-[Pd(OAc)$_2$(P∩P)] (P∩P P = dppe, dppb, dppf, dippf, dtbpf, dcypf, pCF$_3$-dppf, DPEphos, Xantphos). To a suspension of $Pd(OAc)_2$ (0.4 mmol) in acetone (3 mL) a solution of P∩P (0.4 mmol) in acetone (5 mL) was added dropwise within 10 min under stirring at room temperature. A precipitate formed in a few seconds. This suspension was concentrated to half volume and *n*-hexane (20 mL) was added under vigorous stirring. The microcrystalline solid was filtered off, washed with *n*-hexane and dried under vacuum.

cis-[$Pd(OAc)_2$(dppe)]. The general procedure was used except that the ligand was dissolved in acetone/CH_2Cl_2 (1/1, 5 mL). Yield: 98 %. The characterizations were in agreement with those reported in literature, hereafter the main data are presented.[4, 8] IR: ν(OAc) 1613, 1580, 1369, 1319 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.93-7.54 (m, 20H, Ar), 2.25 (m, 4H, CH_2), 1.67 (s, 6H, OAc). $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$, 25 °C): δ 59.15 (s);

cis-[$Pd(OAc)_2$(dppf)]. The general procedure was used except that the ligand was dissolved in acetone/THF (1/1, 5 mL). The characterizations were in agreement with those reported in literature, hereafter the main data are presented.[9] Yield: 89 %. IR: ν(OAc) 1612, 1580, 1364, 1306 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ ppm 7.99-7.39 (m, 20H, Ar), 4.42, 4.39 (s, 8H, Cp), 1.41 (s, 6H, OAc). $^{31}P\{^1H\}$ NMR (161 MHz, CD_2Cl_2, 25 °C): δ 30.8 (s).

cis-[$Pd(OAc)_2$(dippf)]. The general procedure was used except that the ligand was dissolved in acetone/THF (1/1, 5 mL). Yield: 66 %. IR: ν(OAc) 1613, 1574, 1359, 1307 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ ppm 4.66, 4.48 (s, 8H, Cp), 2.50 (m, 4H, *i*Pr), 2.00 (s, 6H, OAc), 1.65, 1.33 (dd, J_{PH} =17.00 Hz, J_{PH} = 7.05 Hz, 24H, *i*Pr). $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$, 25 °C): δ 61.74 (s). MALDI-MS: 583.1 $[M - AcO^-]^+$.

[$Pd(OAc)_2$(dtbpf)]. The general procedure was used except that the ligand was dissolved in THF (5 mL). Yield: 52 %. IR: ν(OAc) 1625, 1310 cm^{-1}. Spectra reveal the presence of isomers in solution. ^1H NMR (400 MHz, CD_2Cl_2, 25 °C): δ ppm 4.93-4.18 (m, 8H, Cp), 1.76-1.12 (m, 42H, OAc, *t*But). $^{31}P\{^1H\}$ NMR (161 MHz, CD_2Cl_2, 25 °C): δ 65.68 (s), 62.81 (s), 45.65 (s). TOF-MS: 639.1 $[M - AcO^-]^+$; 611.8 $[M - 2AcO^- + MeO^-]^+$

cis-[$Pd(OAc)_2$(dcypf)]. Yield: 63 %. IR: ν(OAc) 1620, 1604, 1360, 1297 cm^{-1}. ^1H NMR (400 Mz, CD_2Cl_2, 25 °C): δ ppm 4.62, 4.47 (s, 8H, Cp), 1.95-0.92 (m, 50H, OAc, Cy). $^{31}P\{^1H\}$ NMR (161 MHz, CD_2Cl_2, 25 °C): δ 52.03 (s).

cis-$Pd(OAc)_2$(DPEphos). The general procedure was used except that the ligand was dissolved in THF (5 mL). Yield: 90 %. IR: ν(OAc) 1613, 1581, 1363, 1310 cm^{-1}. ^1H NMR (400 MHz, CD_2Cl_2, 25 °C): δ ppm 7.66-6.12 (m, 28H, Ar), 1.32 (m, 6H, OAc). $^{31}P\{^1H\}$ NMR (161 MHz, CD_2Cl_2, 25 °C): 28.14 ppm. TOF-MS: 704.0 $[M - AcO^-]^+$, 736.1 $[M – (AcO^-) + MeOH]^+$.

cis-$Pd(OAc)_2$(Xantphos). The general procedure was used except that the ligand was dissolved in CH_2Cl_2 (5 mL). Yield: 78 %. IR: ν(OAc) 1568, 1387 cm^{-1}. ^1H NMR (400 MHz,

$CDCl_3$, 25 °C): δ 7.61-6.96 (m, 26H, Ar), 1.79 (s, 6H, $C(CH_3)_2$), 1.71 (m, 6H, OAc). $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$, 25 ºC): δ 28.16 (s).

2.3.2 Synthesis of [$PdCl_2$(P∩P)] (P∩P = pCF_3–dppf, pMeO–dppf, SPANphos). In literature several procedures for the synthesis of these complexes are reported. For instance, *trans*–[$PdCl_2$(SPANphos)] was obtained by reaction of [$PdCl_2$(cod)] (cod = 1,5–cyclooctadiene) with stoichiometric amounts of SPANphos.[2]

We followed a similar procedure but using [$PdCl_2(CH_3CN)_2$] as palladium precursor. To a [$PdCl_2(CH_3CN)_2$] (0.3 mmol) dissolved in 5 mL of CH_2Cl_2 a solution of the ligand (0.3 mmol) in CH_2Cl_2 (5 mL) was added dropwise. After 30 min under stirring at room temperature the solution was concentrated at *ca*. 2 mL and Et_2O (20 mL) was added. The formed microcrystalline solid was filtered off, washed with Et_2O and dried under vacuum.

cis-[$PdCl_2$(*p*CF_3-dppf)]. Yield: 74 %. ^1H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 8.07-7.78 (m, 8H, Ph), 4.58, 4.32 (s, 8H, Cp). $^{31}P\{^1H\}$ NMR (161 MHz, CD_2Cl_2, 25 °C): δ 36.48 (s).

cis-[$PdCl_2$(*p*MeO-dppf)]. Yield: 79 %. ^1H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 7.86-6.97 (m, 16H, Ph), 4.42, 4.23 (s, 8H, Cp), 3.89 (s, 12H, OMe). $^{31}P\{^1H\}$ NMR (161 MHz, CD_2Cl_2, 25 °C): δ 34.33 (s).

trans-[$PdCl_2$(SPANPhos)]. Yield: 85 %. ^1H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 8.03-6.55 (m, 22H, Ar), 6.55 (m, 2H, Ar), 2.70 (d, J_{HH} =13.82 Hz, 2H, H), 2.14 (s, 6H, CH_3), 2.06 (d, J_{HH} =13.82 Hz, 2H, H), 1.50 (s, 6H, CH_3), 1.41 (s, 6H, CH_3). $^{31}P\{^1H\}$ NMR (161 MHz, CD_2Cl_2, 25 °C): δ 28.38 (s).

2.3.3 Synthesis of [$Pd(OH_2)_n(OTs)_{2-n}$(P∩P)] $(TsO)_n$ (n = 0, 1; P∩P = dppe, dppb, dppf, dippf, dtbpf, dcypf, pCF_3–dppf, DPEphos, Xantphos, pMeO–dppf, SPANphos). Two different methods have been employed for the synthesis of these complexes. Method A: the [$Pd(OAc)_2$(P∩P)] complexes is treated with two equivalents of $TsOH{\cdot}H_2O$ to form the title complexes as already proposed by our groups for the synthesis of *cis*–[$Pd(OH_2)$(OTs)(dppp)](TsO).[3] Method B: it has been used the standard already reported procedure of synthesis.[10]

The title complex was formed by treating the [$PdCl_2$(P∩P)] with Ag(OTs). TsO^- is a labile ligand and it can be displaced from the coordination sphere of the palladium by the water, present in the system, forming a cationic *aquo* complex**es**. Indeed in solution the $^{31}P\{^1H\}$ NMR spectra of these *cis* complexes indicates that the two phosphorus atoms are equivalent (singlet signal) probably due to the fast exchange of labile water, TsO^- or solvent. Determining the formation of the cationic or the neutral complexes is crucial for the interpretation of the H_2O[11] and TsO[12] signals in the IR spectra.

Method A. To a suspension of [$Pd(OAc)_2$(P∩P)] (0.2 mmol) in acetone (3 mL) a solution of $TsOH{\cdot}H_2O$ (0.4 mmol) in acetone (3 mL) was added dropwise. After **a** 15 minute stirring at room temperature the solution was concentrated to half volume and *n*–hexane (20 mL) was added under vigorous stirring. The microcrystalline solid formed was filtered off, washed with *n*–hexane and dried under vacuum.

cis-[Pd(OH_2)(OTs)(dppe)](TsO).The characterizations were in agreement with those reported in literature, hereafter the main data are presented.[4] Yield 80 %. IR: ν(OH_2) 3225, ν(TsO) 1242, 1220, 1029, 1004, 998 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.67-6.69 (m, 28H, Ar), 2.51, 2.40 (m, 4H, CH_2), 2.04, 2.03 (s, 6H, CH_3-TsO). $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$, 25 °C): δ 70.95 (s).

cis-[Pd(OH_2)(OTs)(dppb)](TsO). The characterizations were in agreement with those reported in literature, hereafter the main data are presented.[4] Yield 78 %. IR: ν(OH_2) 3245, ν(TsO) 1256, 1219, 1028, 1007, 995 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.65-6.99 (m, 28H, Ar), 3.95 (m, 4H, CH_2), 2.31 (s, 6H, CH_3-TsO), 2.10 (m, 4H, CH_2). $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$, 25 °C): δ 34.61 (s).

cis-[Pd(OH_2)$_2$(dppf)](TsO)$_2$. The characterizations were in agreement with those reported in literature, hereafter the main data are presented.[10b, 13] Yield: 87 %. IR: ν(OH_2) 3422, ν(TsO) 1222, 1031, 1007, 998 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.98 - 6.89 (m, 28H, Ar), 4.70, 4.53 (s, 8H, Cp), 2.33 (bs, H_2O), 2.27 (s, 6H, CH_3-TsO). $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$, 25 °C): δ 45.71 (s).

cis-[Pd(OH_2)(OTs)(dippf)](TsO).The characterizations were in agreement with those reported in literature, hereafter the main data are presented. [10c] Yield: 66%. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.63-7.11 (m, 8H, Ar), 4.83, 4.63 (s, 8H, Cp), 2.71 (m, 4H, *i*Pr), 2.35 (s, 6H, CH_3-TsO), 1.73, 1.39 (dd, J_{PH} =16.93 Hz, J_{PH} = 9.89 Hz, 24H, *i*Pr). $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$, 25 °C): δ 83.77 (s). MALDI-MS: 695.1 $[M - H_2O - TsO^-]^+$.

cis-[Pd(OH_2)(OTs)(dtbpf)](TsO). Yield: 82 %. IR: ν(H_2O) 3394, ν(TsO) 1279, 1239, 1031, 1007, 983 cm^{-1}. ^1H NMR (500 MHz, CD_2Cl_2, –70 °C): δ 7.77-7.22 (m, 8H, Ar), 5.06,4.86 (m, 8H, Cp), 2.41 (s, 6H, CH_3-TsO), 1.70-1.19 (m, 36H, *t*But). $^{31}P\{^1H\}$ NMR (201 MHz, CD_2Cl_2, -70 ºC): δ 90.95 (s). TOF-MS: 615.8 $[M – (2\ TsO^-)+(OH^-)]^+$; 635.1 $[M – (2\ TsO^-)+(OH^-)(MeO^-)+Li^+]^+$.

cis-[Pd(OTs)$_2$(dcypf)]. Yield: 75 %. IR: ν(OTs) 1234, 1030, 1007 cm^{-1}. ^1H NMR (500 MHz, CD_2Cl_2, -70 °C): δ 7.74, 7.19 (s, 8 H, Ar), 4.82, 4.64 (s, 8H, Cp), 2.40 (s, 6H, CH_3-TsO), 1.85-1.30 (m, 44H, Cy). $^{31}P\{^1H\}$ NMR (201 MHz, CD_2Cl_2, -70 ºC): δ 76.89 (s).

cis-[Pd(OTs)$_2$(*p*CF_3-dppf)]. Yield: 71 %. IR: ν(OTs) 1249, 1030, 1004 cm^{-1}. ^1H NMR (500 MHz, CD_2Cl_2, -70 °C): δ 8.22-7.05 (s, 24H, Ar), 4.70, 4.49 (s, 8H, Cp), 2.40 (s, 6H, CH_3-TsO). $^{31}P\{^1H\}$ NMR (201 MHz, CD_2Cl_2, -70 ºC): δ 37.14 (s).

cis-[Pd(OH_2)(OTs)(DPEphos)](TsO). Yield: 82 %. IR: ν(TsO) 1218, 1029, 997 cm^{-1}. ^1H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 7.65-6.73 (m, 36H, Ar), 2.36 (s, 6H, CH_3-TsO). $^{31}P\{^1H\}$ NMR (161 MHz, CD_2Cl_2, 25 ºC): δ 29.50 (s). TOF-MS: 694.0 $[M – (2\ TsO^-)+(MeO^-)]^+$;

cis-[Pd(OH_2)(OTs)(Xantphos)](TsO). Yield: 70 %. IR: ν(OH_2) 3438, ν(TsO) 1257, 1227, 1034, 1011, 1001 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.60-6.97 (m, 34H, Ar), 2.28 (s, 6H, CH_3-TsO), 1.82 (s, 6H, $C(CH_3)_2$). $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$, 25 ºC): δ 45.23 (s).

Method B. Ag(OTs) (0.2 mmol) was dissolved in 10 mL of MeOH with the exclusion of light and [$PdCl_2$(P∩P)] (0.1 mmol) dissolved in 10 mL of CH_2Cl_2 was added to the solution . The mixture was stirred at room temperature for 2 h. AgCl was filtered off through Celite and the solvent was evaporated under reduced pressure. The crude solid was dissolved again in acetone (*ca*.

1–2 mL) and by addition of *n*–hexane (20 mL) a microcrystalline solid was formed. The solid was filtered off, washed with n–hexane and dried under vacuum.

cis-[Pd(OTs)$_2$(*p*MeO-dppf)]. Yield: 78 %. IR: ν(OTs) 1255, 1027, 1009 cm^{-1}. ^{1}H NMR (500 MHz, CD_2Cl_2, -70 °C): δ 7.85-6.96 (s, 24H, Ar), 4.66, 4.56 (s, 8H, Cp), 3.88 (s, 12H, CH_3O), 2.34 (s, 6H, CH_3-TsO). ^{31}P{^{1}H} NMR (201 MHz, CD_2Cl_2, -70 °C): δ 45.44 (s).

trans-[Pd(OTs)$_2$(SPANPhos)]. Yield: 80 %. IR: ν(OTs) 1223, 1030, 1009 cm^{-1} ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 8.05-6.91 (m, 32H, Ar), 2.36 (s, 6H CH_3-TsO), 2.31 (s, 6H, CH_3), 2.27 (d, J_{HH} =14.17 Hz, 2H, H), 1.53 (d, J_{HH} =14.17 Hz, 2H, H), 1.30 (s, 6H, CH_3), 1.26 (s, 6H, CH_3). ^{31}P{^{1}H} NMR (161 MHz, CD_2Cl_2, 25 ºC): δ 38.13 (s).

2.3.4 Synthesis of cis–[Pd(C_2O_4)(dppf)]. To a suspension of *cis*–[Pd(OAc)$_2$(dppf)] (0.25 mmol) in ethanol (8 mL) a solution of $H_2C_2O_4 \cdot 2H_2O$ (0.28 mmol) in acetone (5 mL) was added dropwise under stirring. After 20 minutes Et_2O (20 mL) was added to the solution and the formed microcrystalline solid was filtered off, washed with H_2O, Et_2O and dried under vacuum. Yield: 80 %. IR: ν(C_2O_4) 1697, 1676, 1357, 780 cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 7.77-7.47 (m, 20H, Ar), 3.72, 3.58 (s, 8H, Cp). ^{31}P{^{1}H} NMR (161 MHz, CD_2Cl_2, 25 ºC): δ 34.04 ppm. Elem anal. Calcd for $C_{36}H_{28}O_4P_2FePd$: C, 57.74; H, 3.77; Found: C, 57.76 ; H, 3.99.

2.3.5 Synthesis of cis–[Pd(SO_4)(dppf)]·H_2O. To a suspension of [Pd(OAc)$_2$(dppf)] (0.25 mmol) in ethanol (3 mL) a solution of H_2SO_4 (0.3 mmol) in ethanol (1 mL) was added dropwise under stirring. After 20 minutes 20 mL of Et_2O were added to the solution, and the formed microcrystalline solid was filtered off, washed with Et_2O and dried under vacuum. Yield: 86 %. IR: ν(H_2O) 3656, 3495, ν(SO_4) 1260, 1142, 1099, 897 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.75-7.47 (m, 20H, Ar), 4.54, 4.40 (s, 8H, Cp), 1.58 (br, H_2O). ^{31}P{^{1}H} NMR (161 MHz, $CDCl_3$, 25 ºC): δ 41.71 ppm. Elem anal. Calcd for $C_{34}H_{30}O_5P_2SFePd$: C, 52.70; H, 3.90; S, 4.13; Found: C, 52.89; H, 3.65; S, 4.05.

2.3.6 Synthesis of cis–[Pd(COOMe)$_2$(P∩P)] (P∩P = dppe, dppp). *cis*–[Pd(OH_2)(OTs)(P∩P)](TsO) (0.1 mmol) was dissolved in 2 mL of MeOH and the solution was pressurized with carbon monoxide (2 atm) at 0 °C for 10 minutes under stirring. The reaction mixture turned from yellow to brown. NEt_3 (0.8 mmol) were then added while stirring 10 more minutes. The light brown solid formed was collected on a filter, washed with MeOH, Et_2O and dried under vacuum.

cis-[Pd(COOMe)$_2$(dppe)]. Yield: 80 %. IR: ν(C=O) 1627, 1653 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.97-7.27 (m, 20H, Ar), 3.47 (s, 6H OCH_3), 2.38-2.32 (m, 4H, CH_2). ^{31}P{^{1}H} NMR (161 MHz, $CDCl_3$, 25 ºC): δ 38.8 ppm. Elem anal. Calcd for $C_{30}H_{30}O_4P_2Pd$: C, 57.84; H, 4.85; Found: C, 58.18 ; H, 4.95.

cis-[Pd(COOMe)$_2$(dppp)]. Yield: 86 %. IR: ν(C=O) 1622, 1647cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 7.56-7.38 (m, 20H, Ar), 3.00 (s, 6H OCH_3), 2.50 (m, 4H, CH_2), 1.89 (m, 2H,

CH_2) ppm. $^{31}P\{^1H\}$ NMR (161 MHz, CD_2Cl_2, 25 °C): δ 0.25 ppm. Elem anal. Calcd for $C_{31}H_{32}O_4P_2Pd$: C, 58.46; H, 5.06; Found: C, 57.82; H, 5.18.

2.3.7 Synthesis of trans–[Pd(COOMe)(OTs)(SPANphos)]. A 5 mm sapphire HPNMR tube was charged under Ar with a solution of *trans*–[$Pd(OTs)_2$(SPANphos)] (5 mg, 0.004 mmol) in 0.5 mL of CD_2Cl_2 with 10 % of MeOH and then pressurized with 10 atm of CO at –78 °C. NMR analyses reveal the formation of the title complex. ^1H NMR (500 MHz, CD_2Cl_2/MeOH 10%, -78 °C): δ 7.66-7.21 (m, 32H, Ar), 3.13 (s, 3H, $COOCH_3$), 2.35 (s, 6H, CH_3-TsO), 2.16 (s, 6H, CH_3), 2.08 (m, 2H, H), 1.53-1.19 (m, 12H, H + CH_3). $^{31}P\{^1H\}$ NMR (201 MHz, CD_2Cl_2/MeOH 10%, 25 ºC): δ 15.92 (d, J_{PP} =180 Hz), 9.19 (d, J_{PP} = 180 Hz).

2.4 In situ NMR study on the preparation of [Pd(COOMe)$_2$(P∩P)] (P∩P = dppe, dppp, dppb, dppf, DPEphos, Xantphos, SPANphos) by exchange reaction.

A solution of *cis*–[$Pd(COOMe)_2$(dipy)] (2.5 mg, 0.007 mmol) in 0.2 mL of CD_2Cl_2 was charged in a NMR tube under Ar. To this mixture, at –78 °C, a solution of the desired P∩P (0.007 mmol) dissolved in 0.2 mL of CD_2Cl_2 was added. The exchange reaction was followed by $^{31}P\{^1H\}$and ^1H NMR spectroscopy. When with dppf the solution was prepared in a 5 mm sapphire HPNMR tube which was then pressurized with 30 atm of CO at –78°C. The reaction was followed by variable–temperature $^{31}P\{^1H\}$and ^1H NMR spectroscopy.

2.5 Carbonylation procedures.

Typically, 5 mL of a solution of *i*PrOH and NEt_3 was introduced into a *ca*.15 mL glass bottle, previously evacuated by Ar flow, containing 0.001 mmol of catalyst precursor and the desired amount of BQ. The glass bottle was then placed in an autoclave of *ca*. 50 mL volume, previously evacuated by a vacuum pump, under Ar flow. The autoclave was first purged several (4–5) times with CO, then pressurized and heated to the desired pressure and temperature. The solution was stirred with a magnetic bar. After the desired reaction time**,** the autoclave was rapidly cooled to 0 °C and slowly depressurized. The solution was analyzed by GC using *n*–undecane and toluene as internal standard.

3. References

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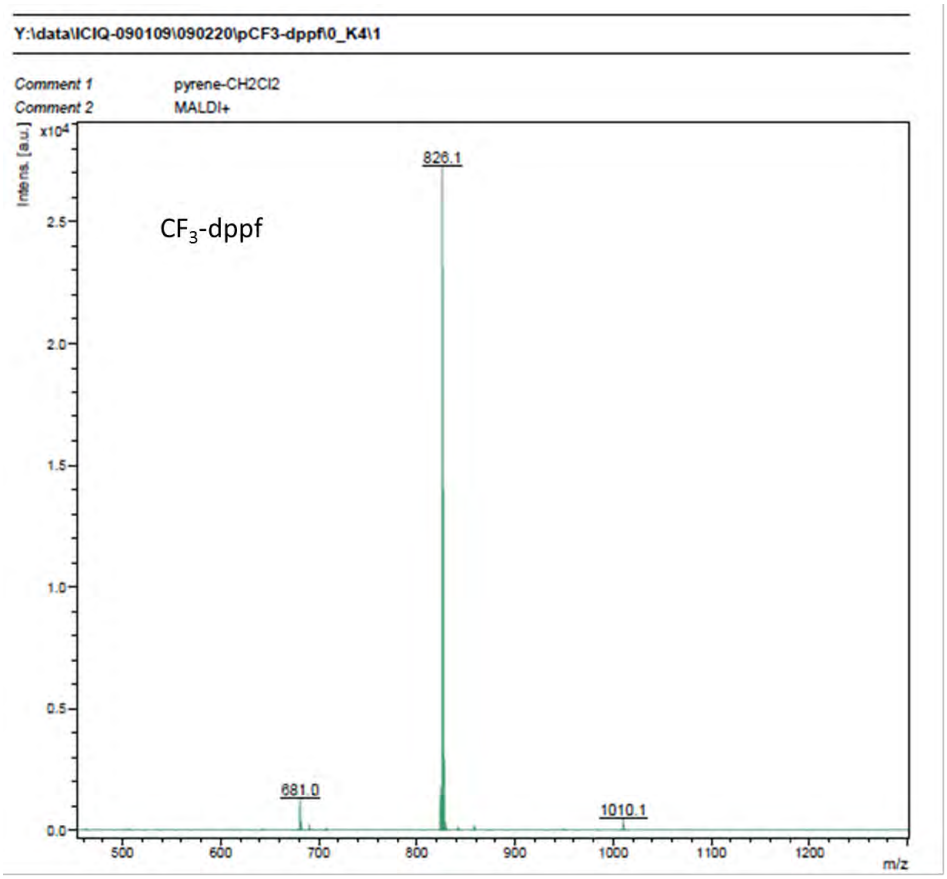
4. Spectra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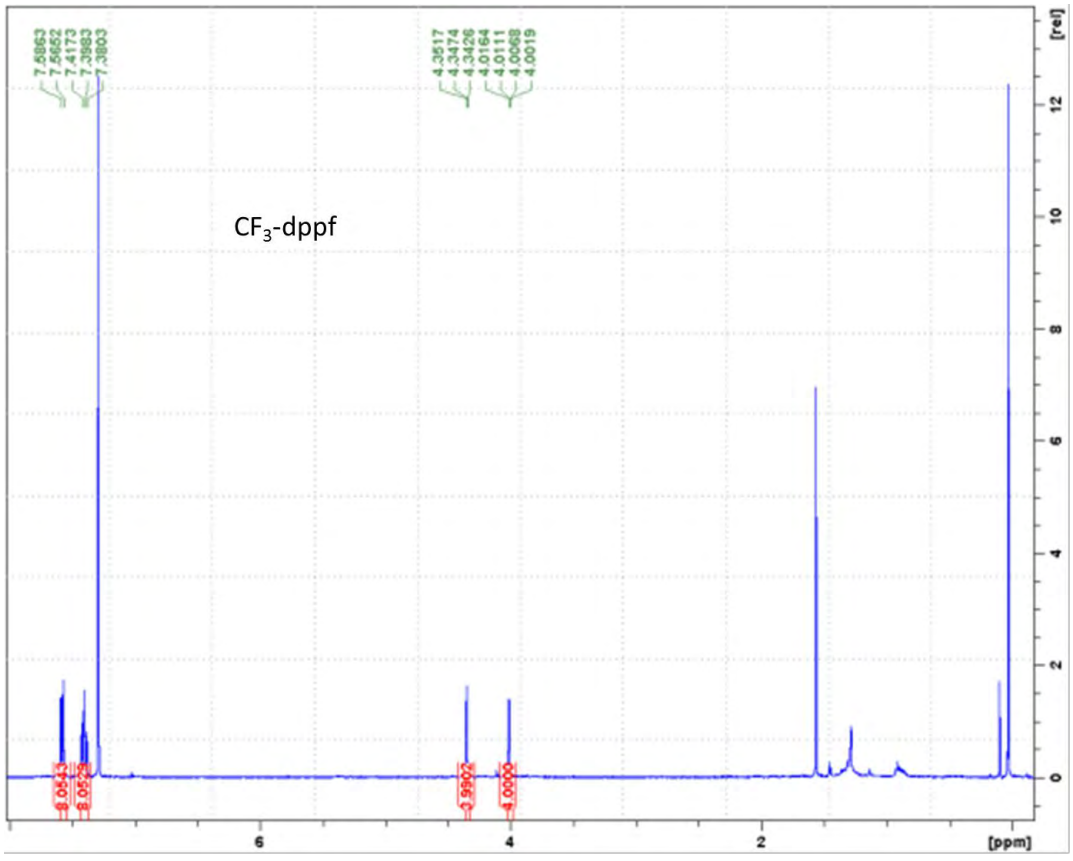
1010.1
CF3-dppf
m/z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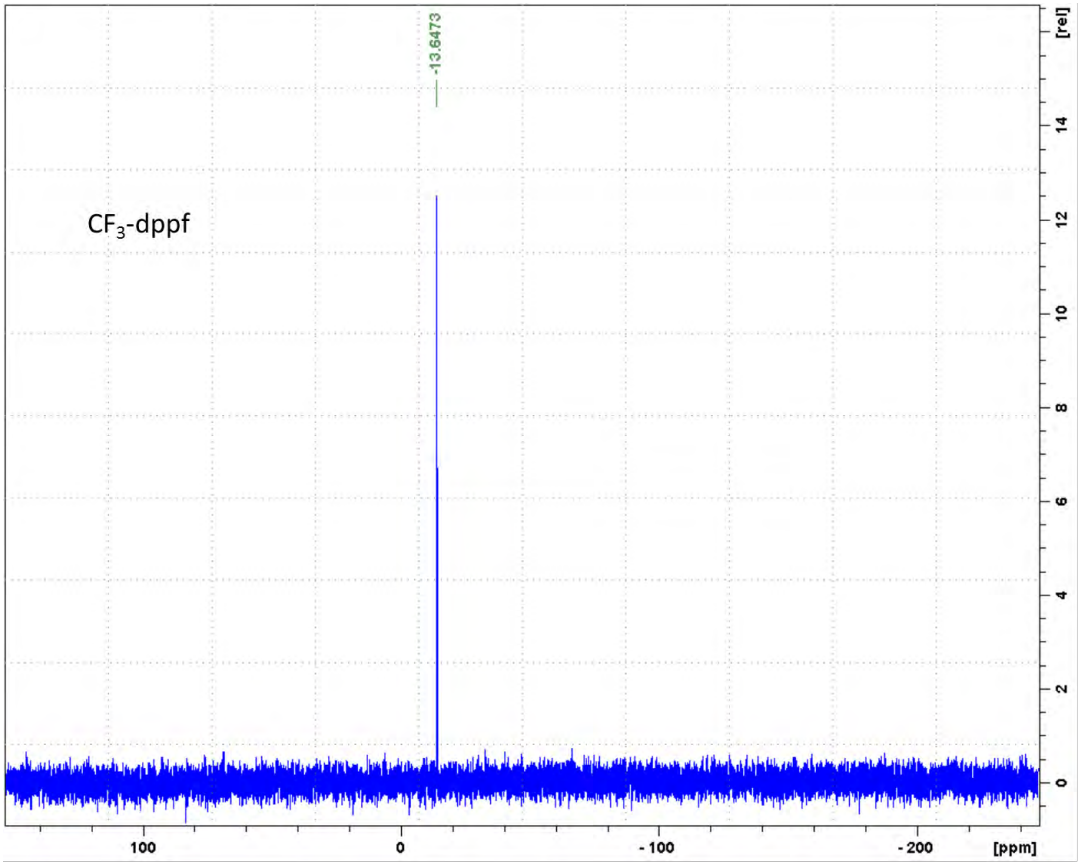
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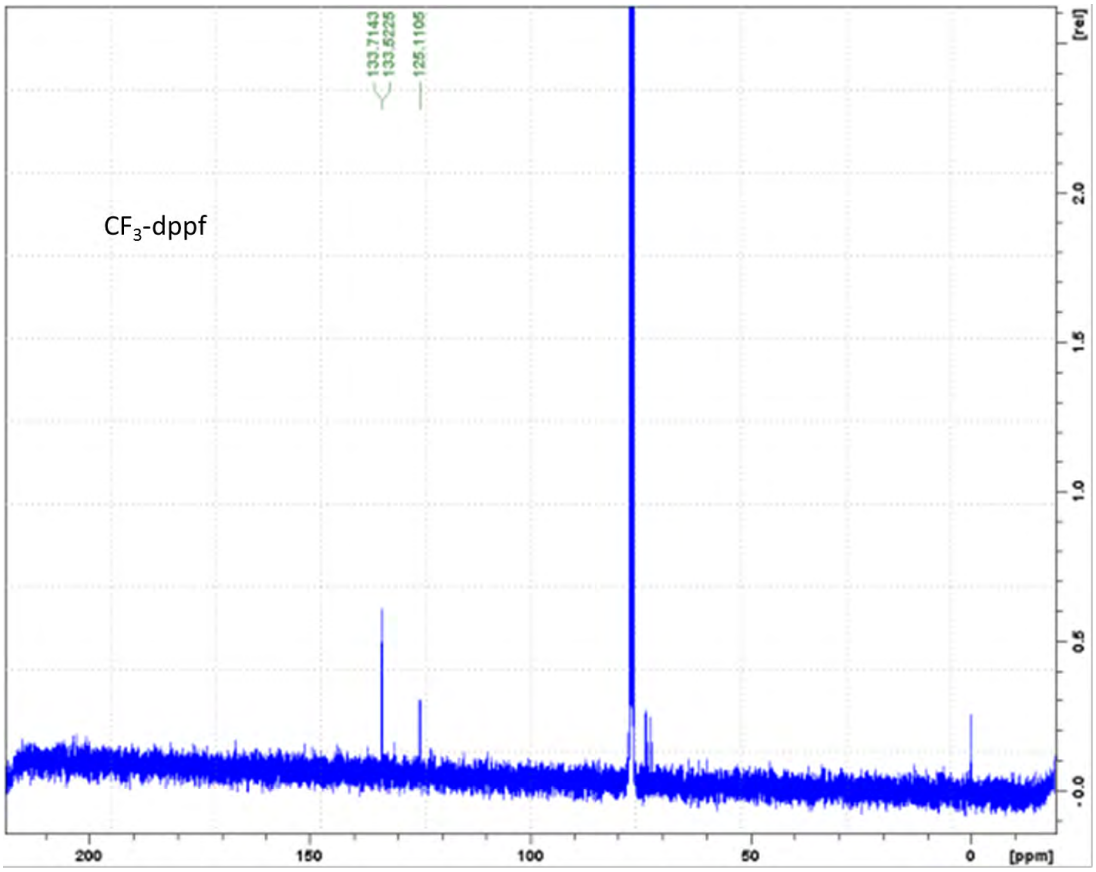
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100
50
0
[ppm]

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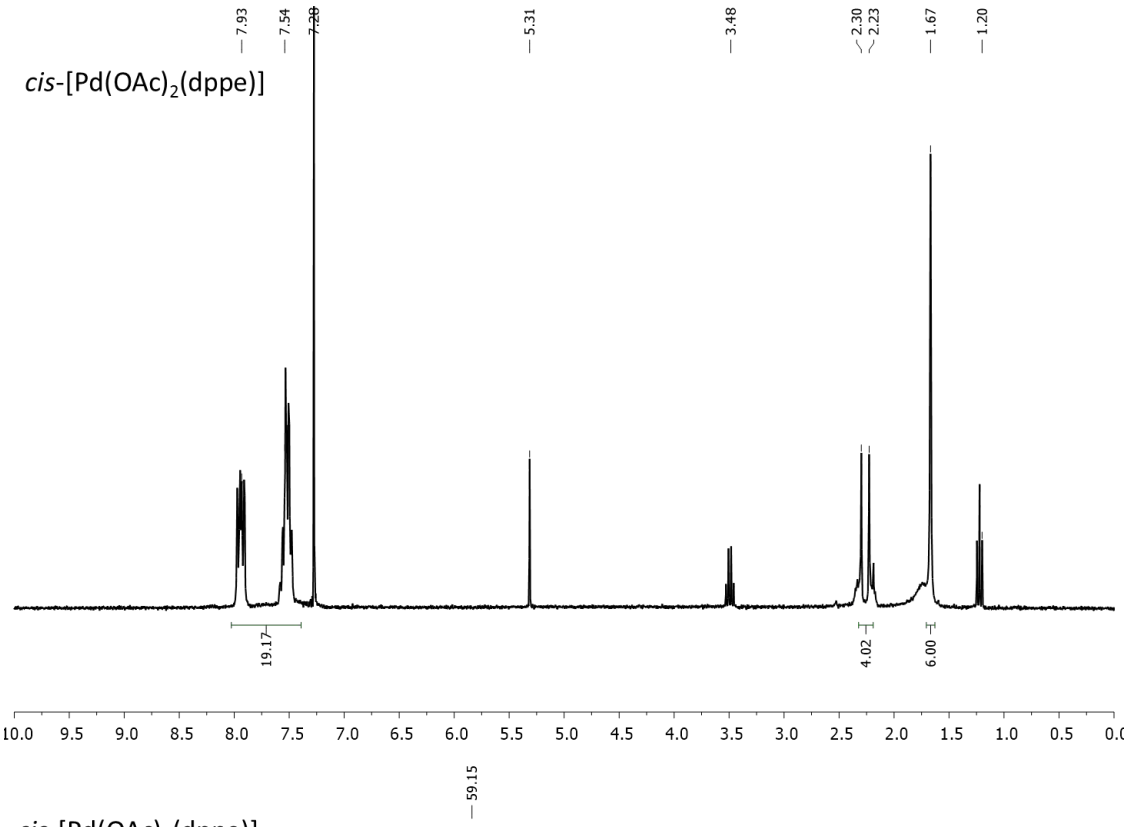

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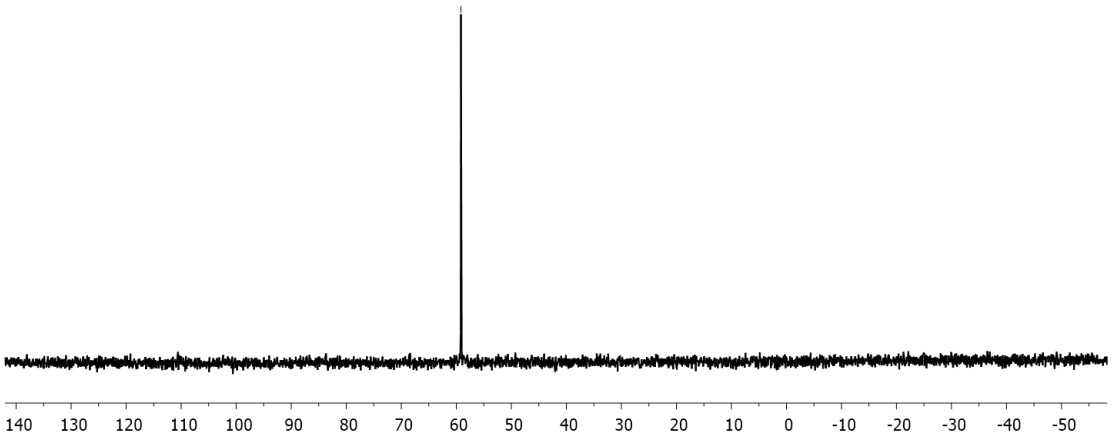

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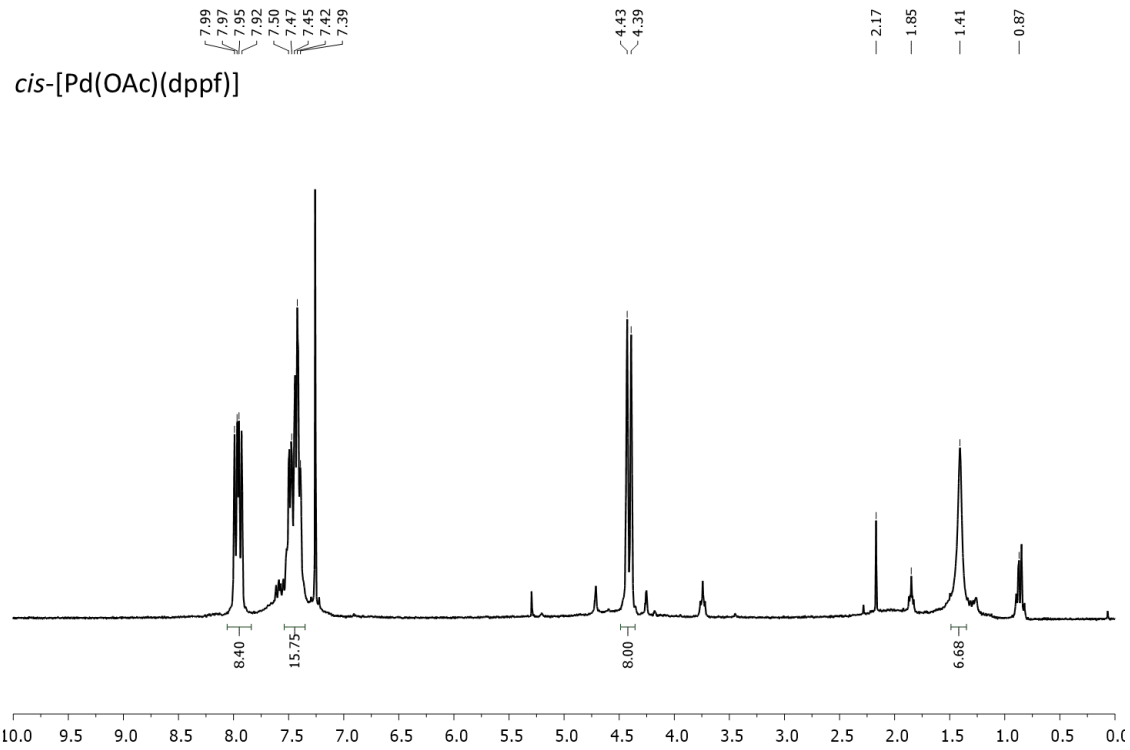

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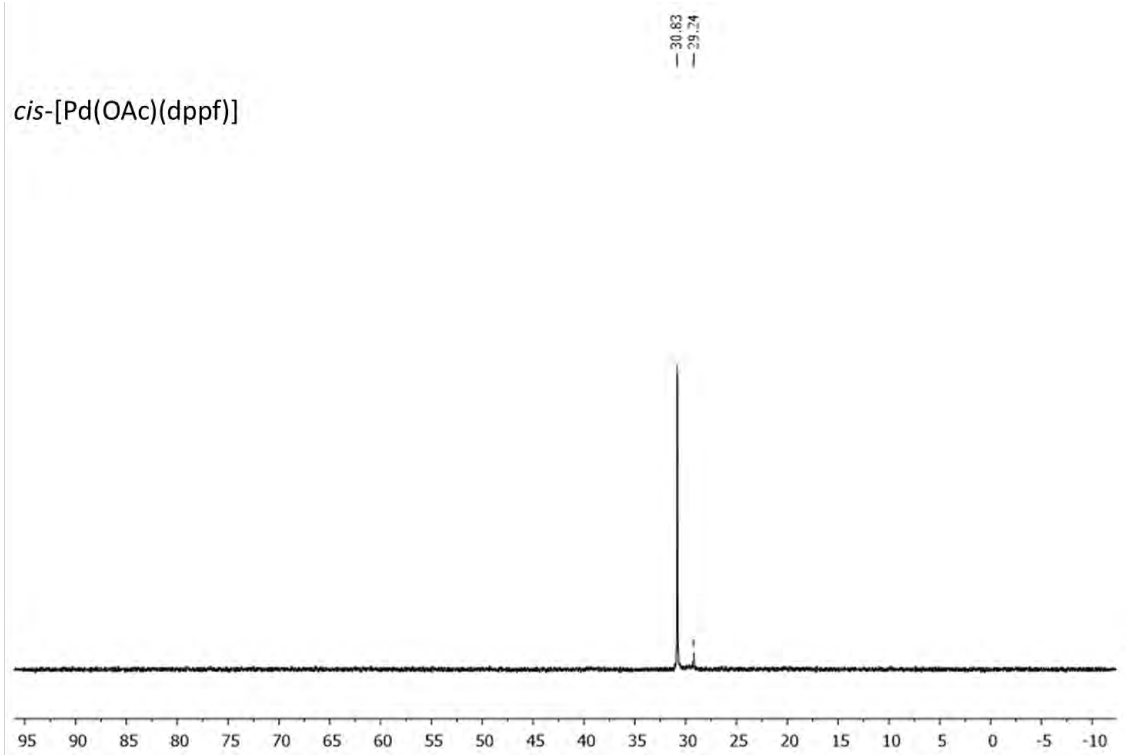

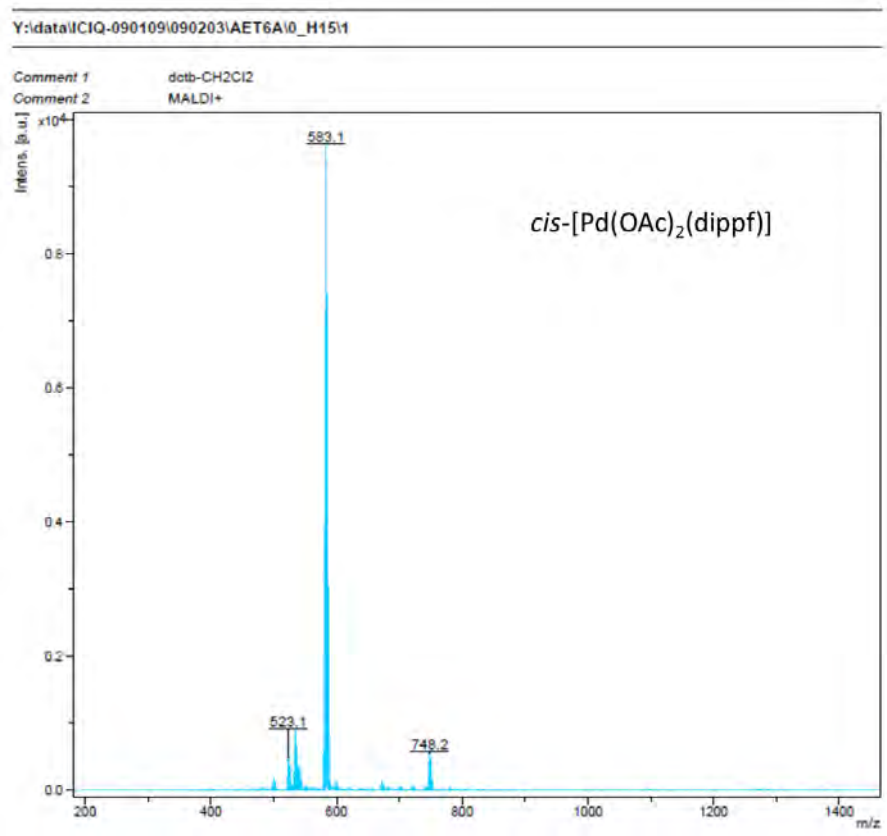
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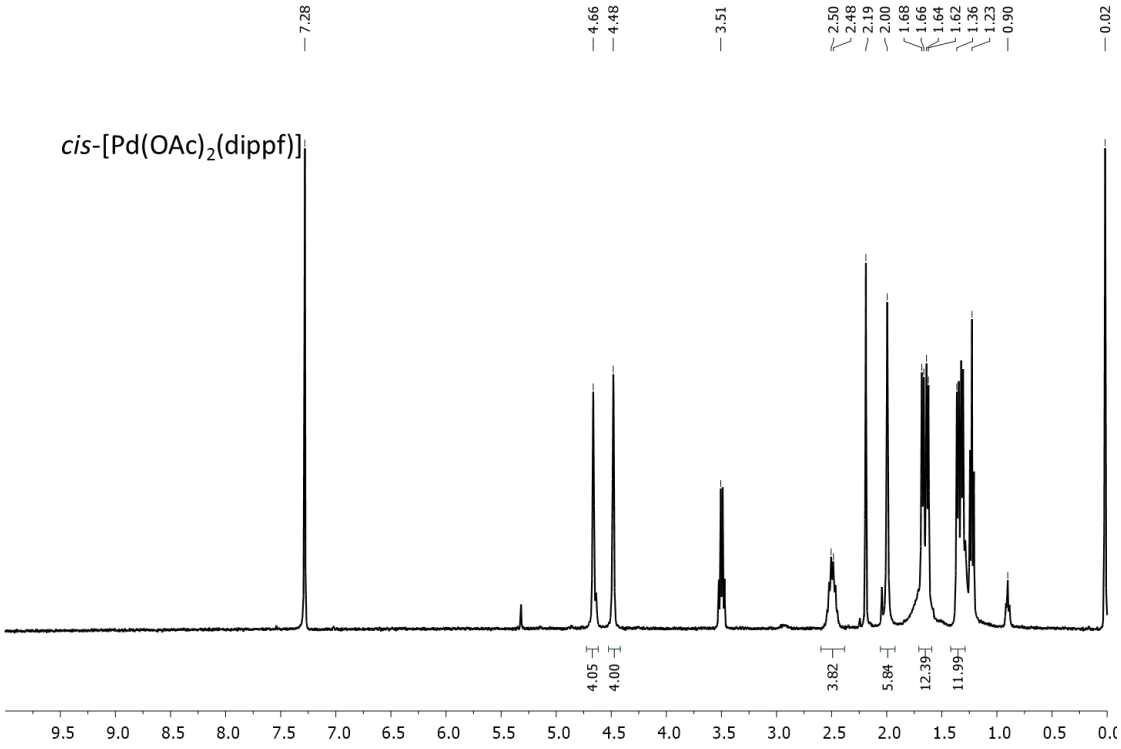
523.1
748.2
cis-[Pd(OAc)2(dippf)]
m/z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4.66
4.48
3.51
2.50
2.48
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1.66
1.64
1.62
1.36
1.23
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cis-[Pd(OAc)2(dippf)]
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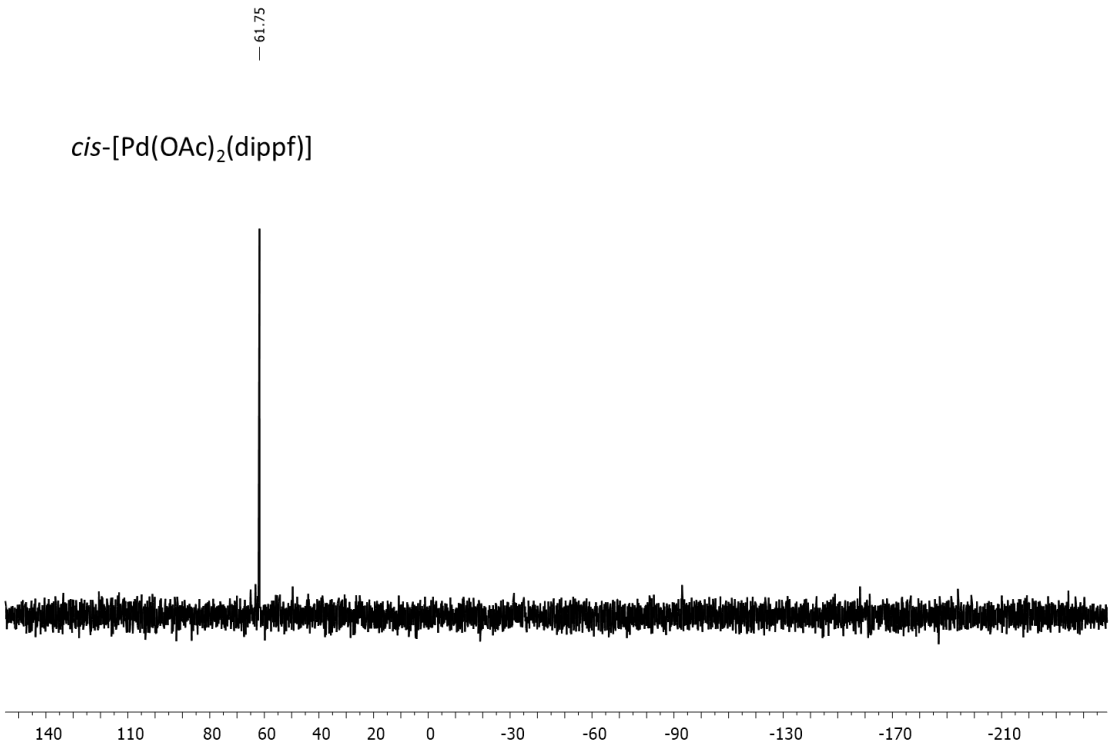
12.39
11.99



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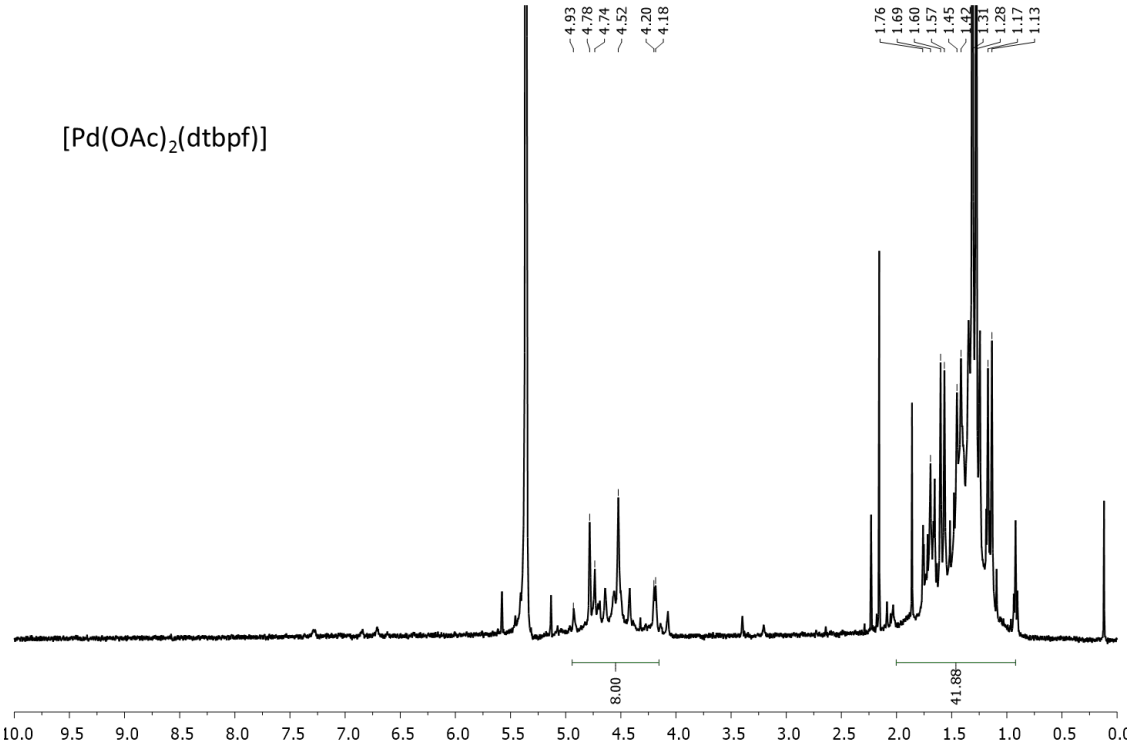
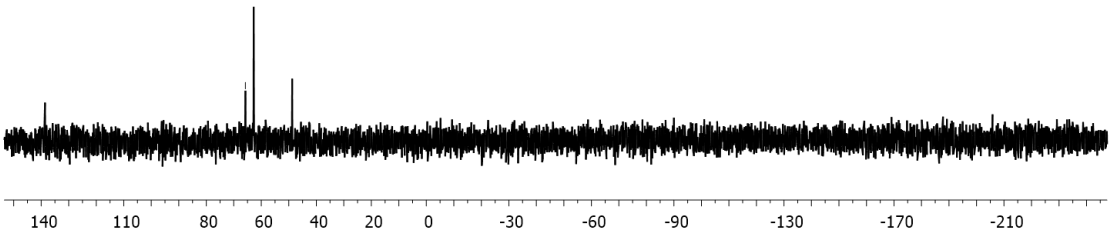
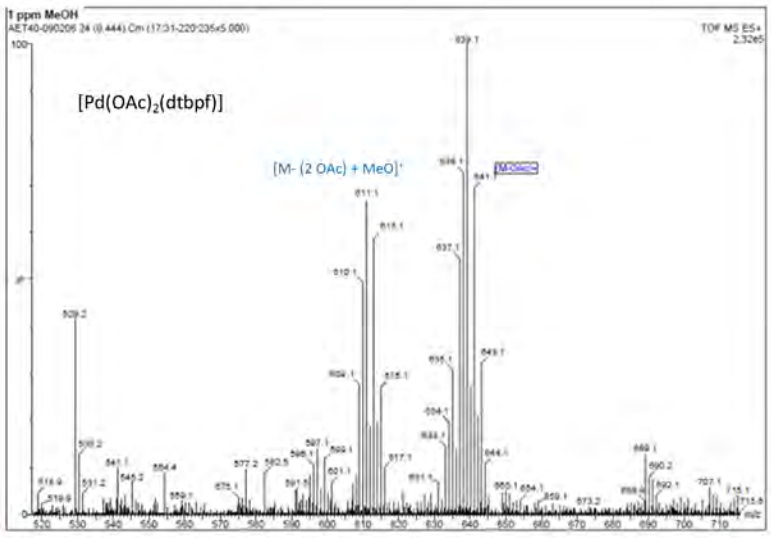


[Pd(OAc)$_2$(dtbpf)]

65.78
62.84
48.65

[Pd(OAc)$_2$(dtbpf)]

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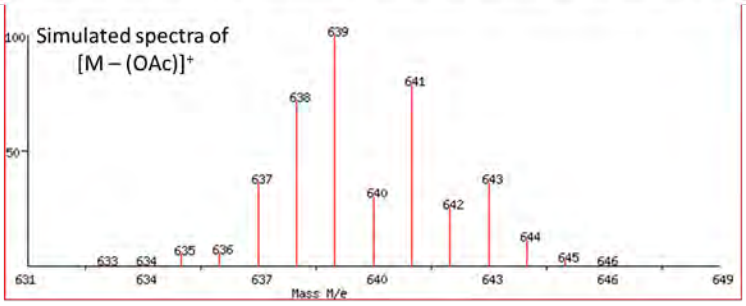
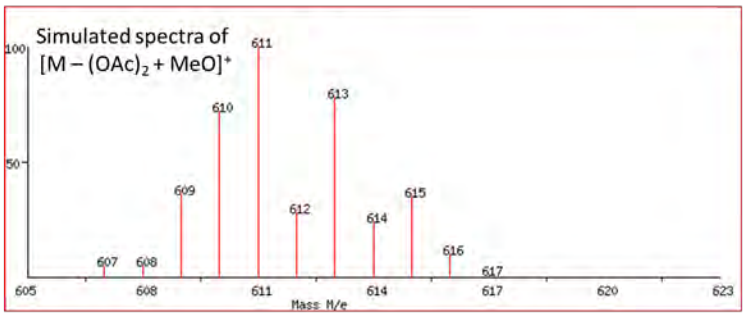

Simulated spectra of
[M – (OAc)]+
Mass M/e


Simulated spectra of
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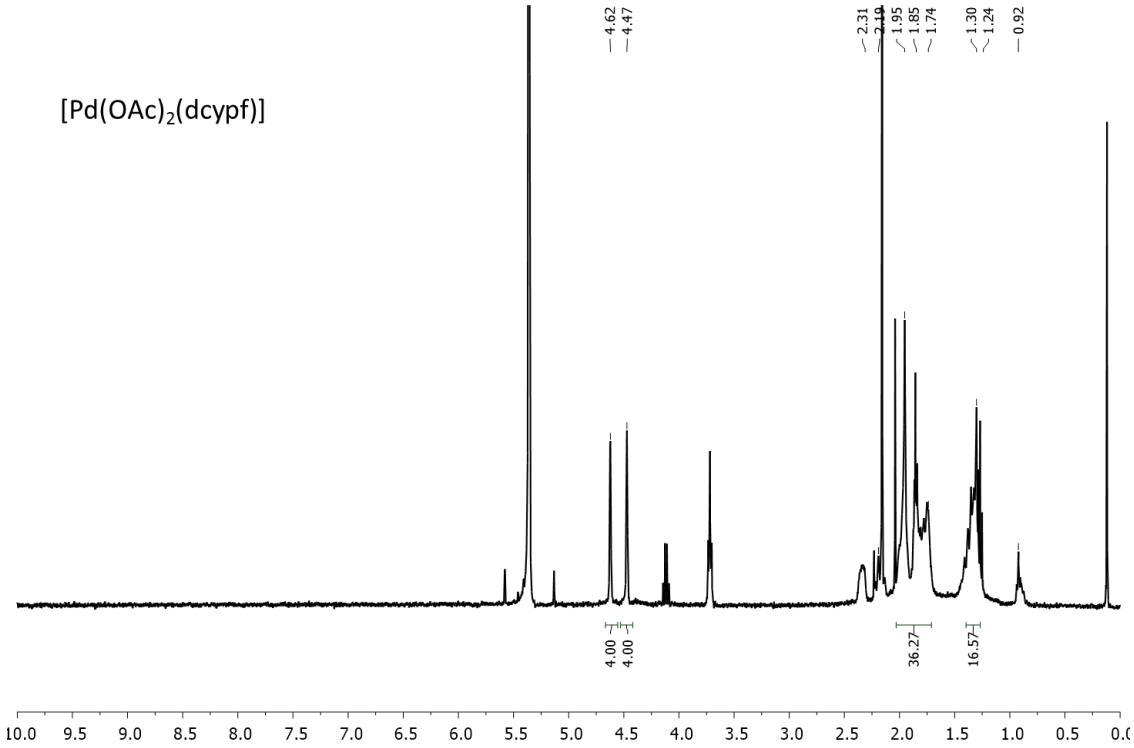
Mass M/e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1.24
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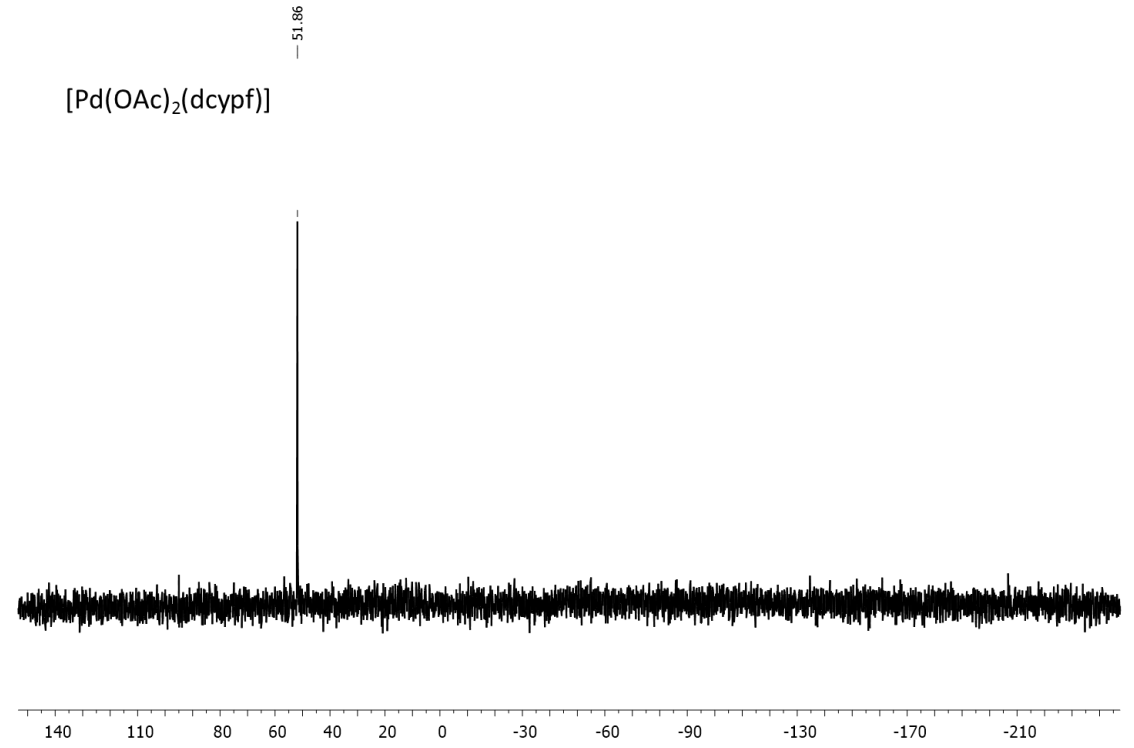
4.00
4.00
36.27
16.57
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5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[Pd(OAc)2(dcypf)]
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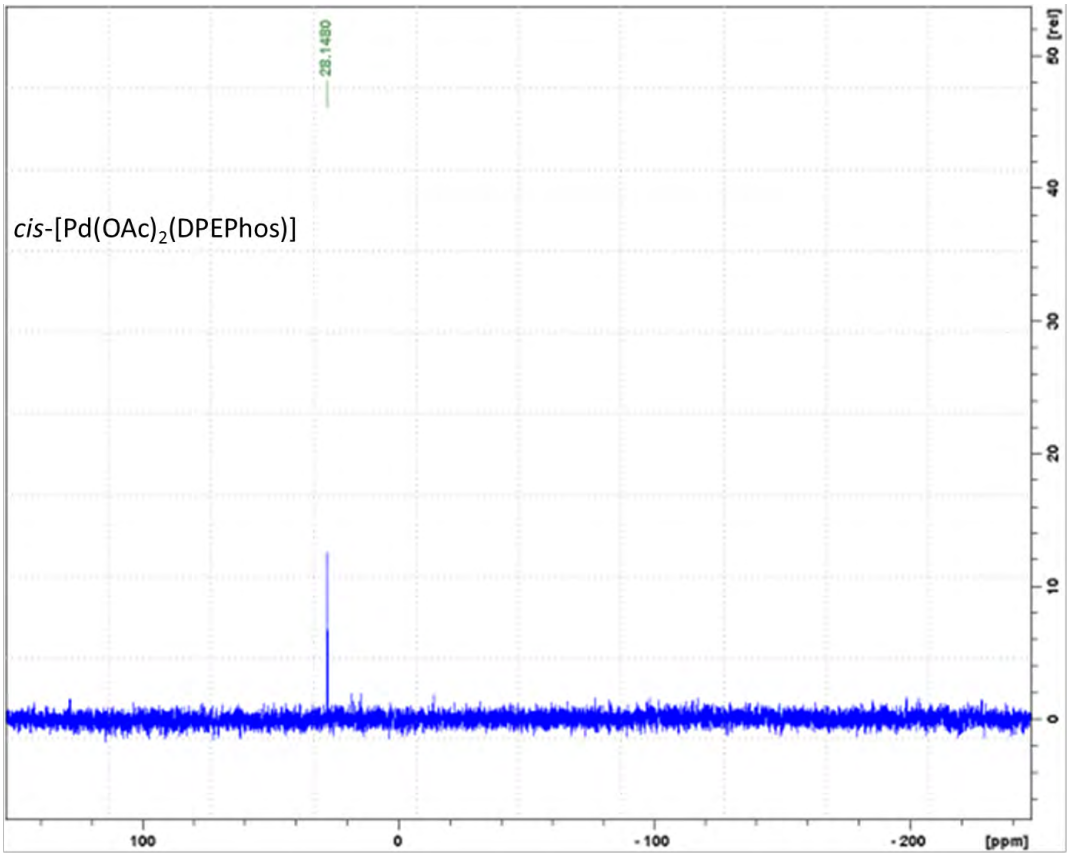
28.1480
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40
30
20
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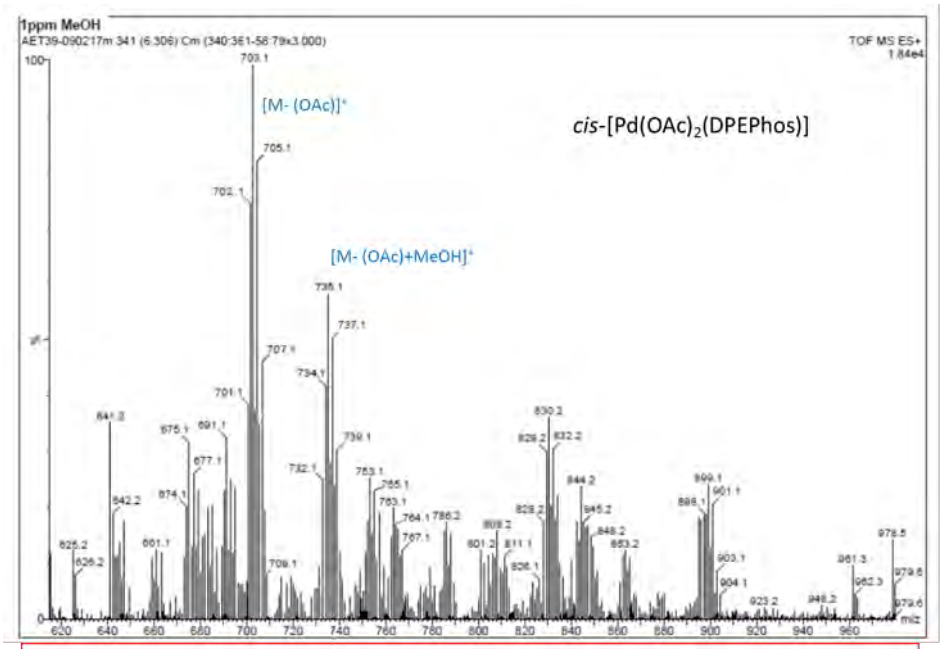
0
-100
-200
[ppm]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TOF MS ES+
[M- (OAc)]+
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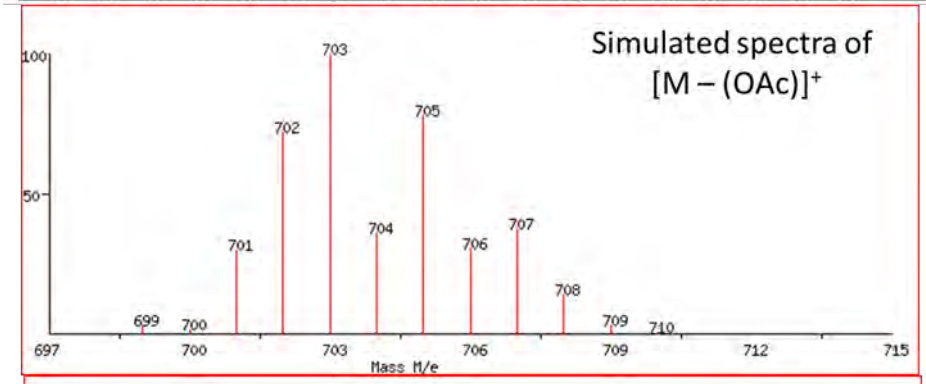
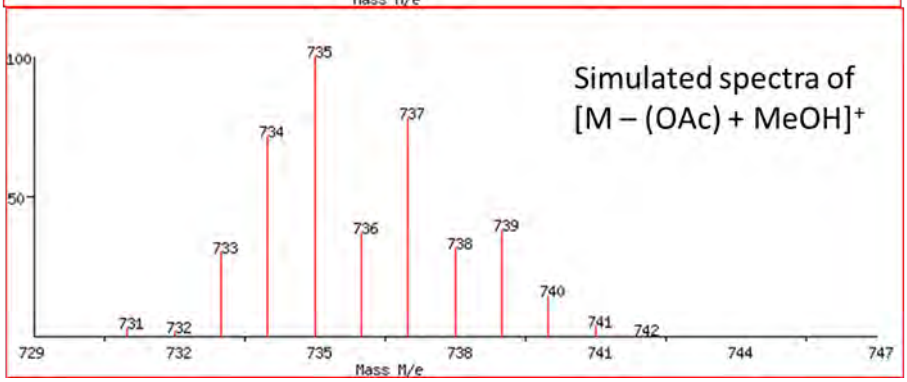
m/z


Simulated spectra of
[M – (OAc)]+
Mass M/e


Simulated spectra of
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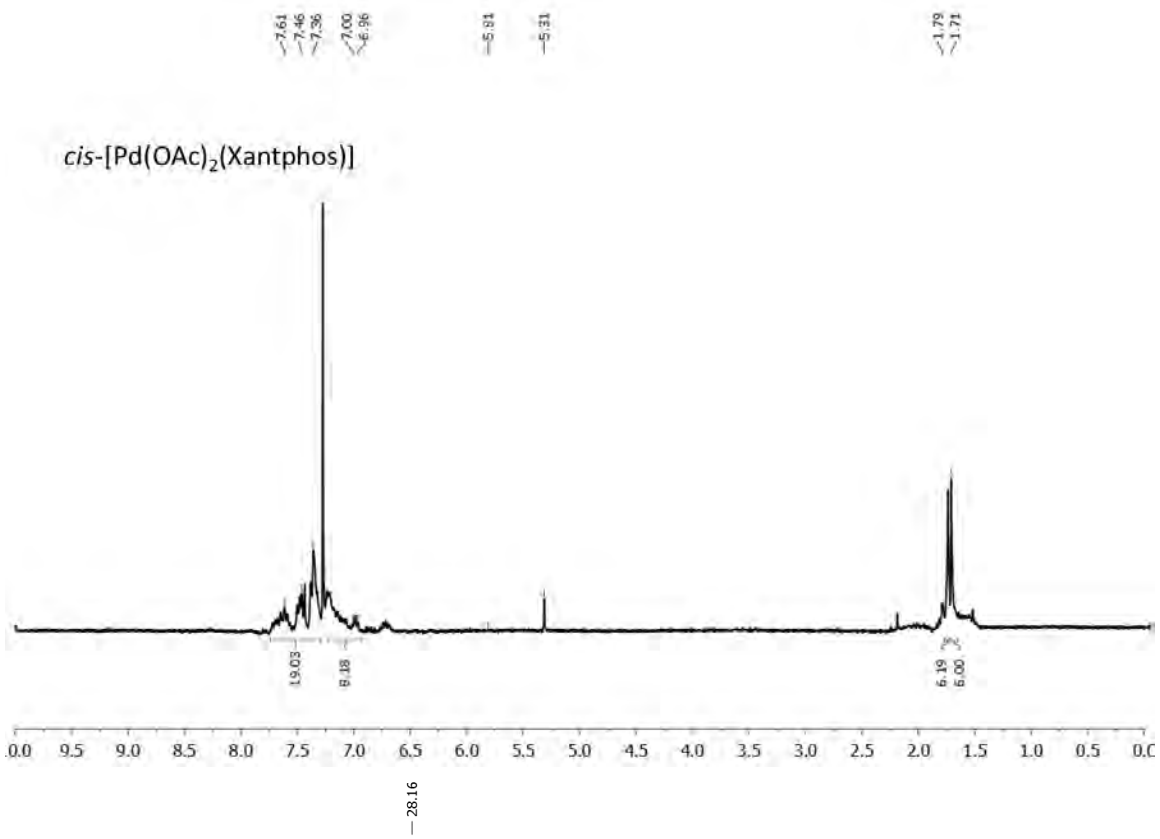
Mass M/e



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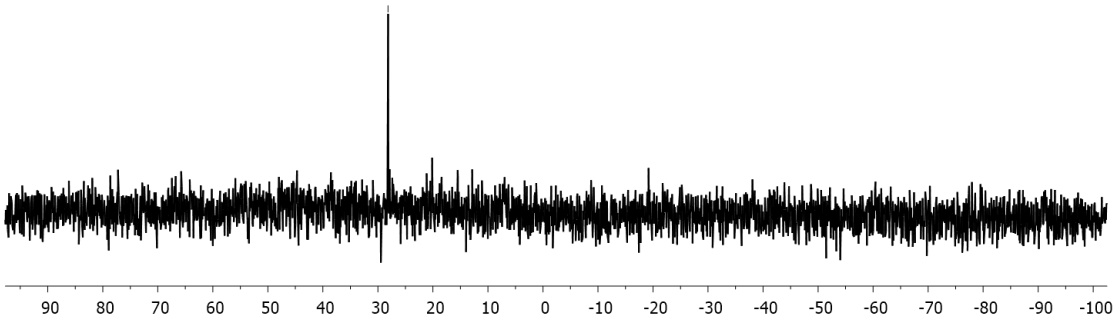

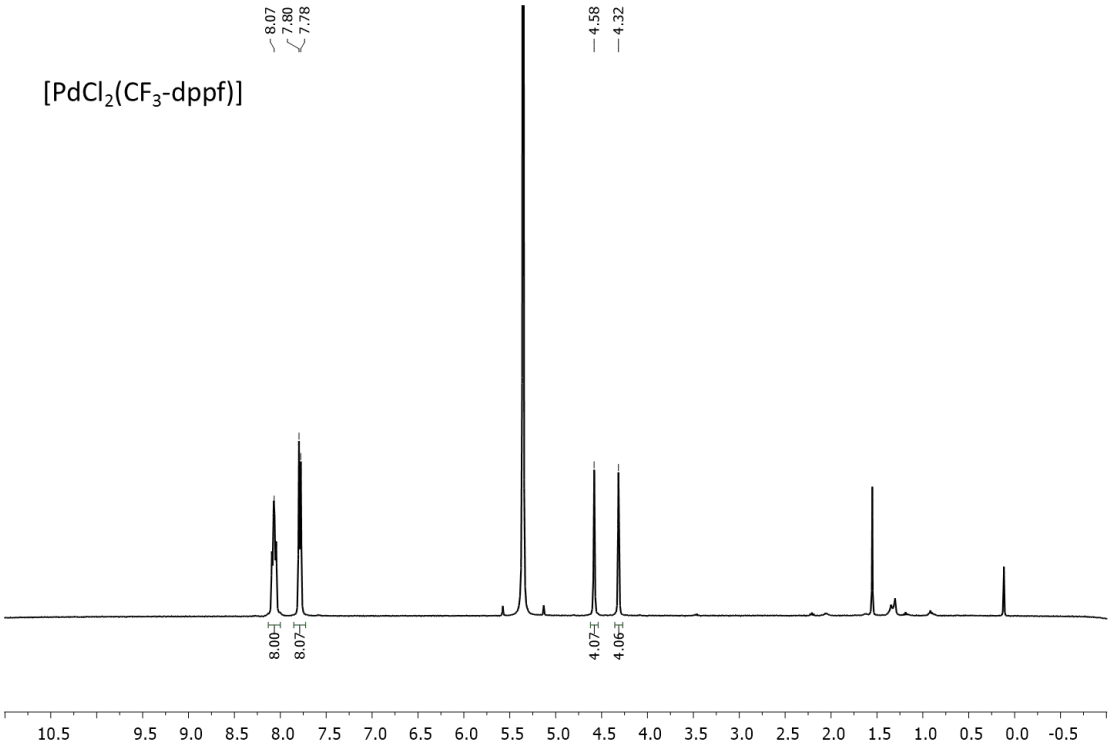
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4.06
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.0
3.5
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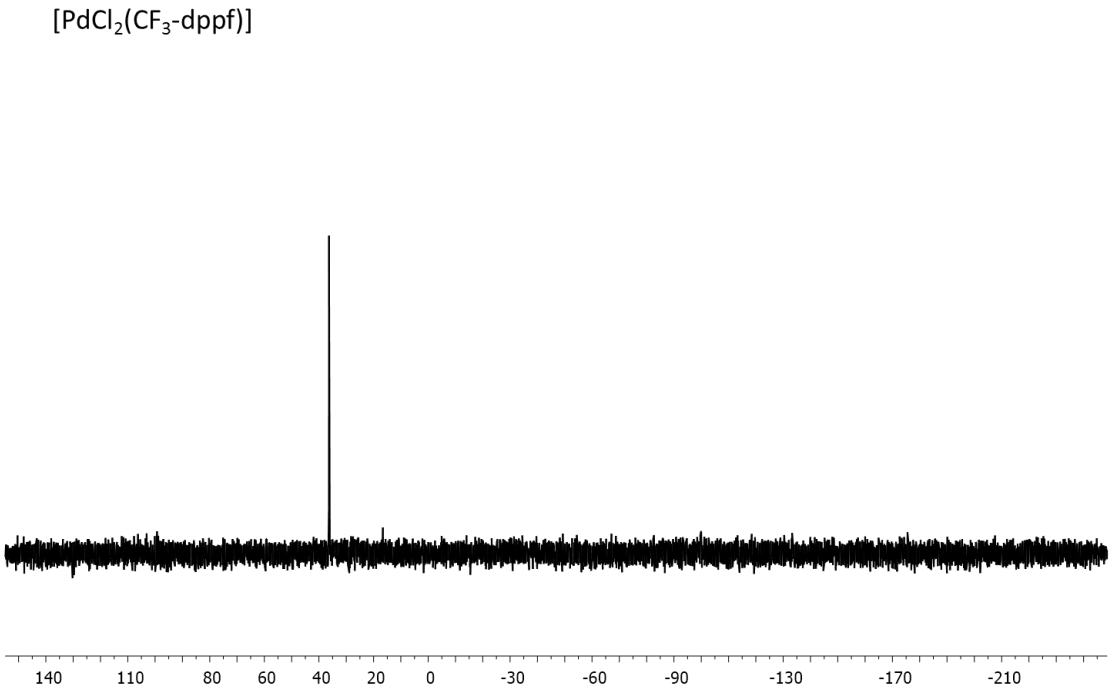
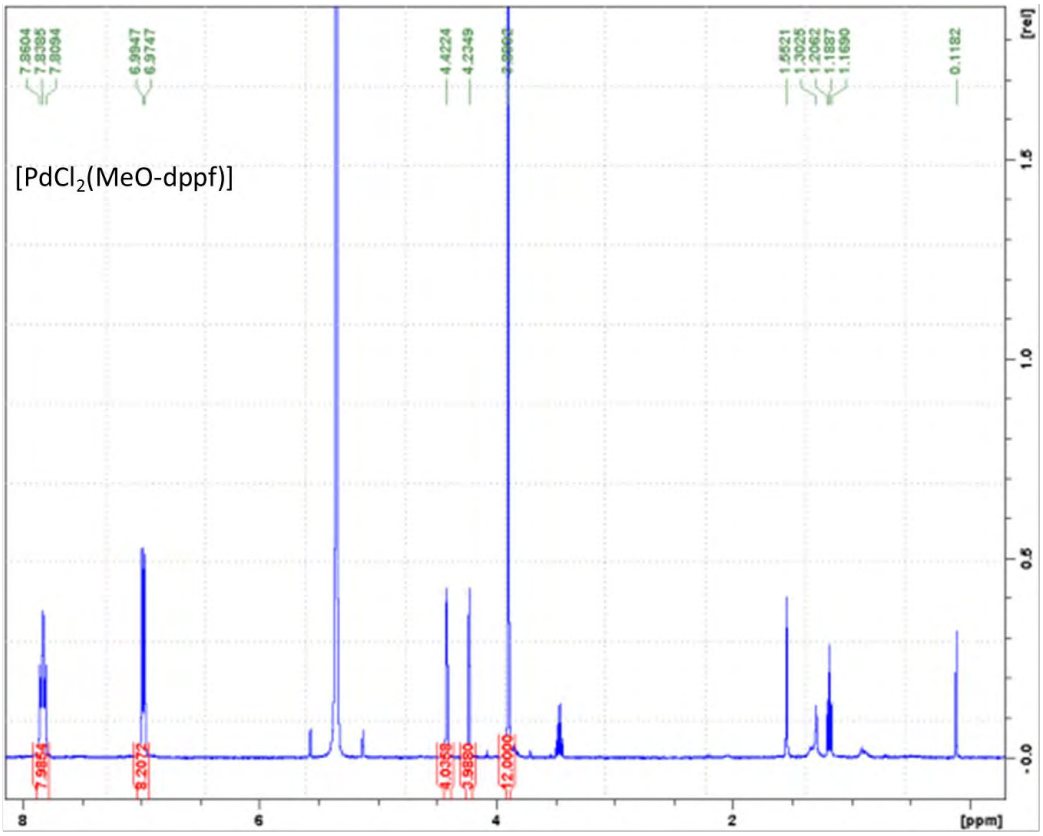
2.5
2.0
1.5
1.0
0.5
0.0
-0.5


[PdCl2(CF3-dppf)]
140
110
80
60
40
20
0
-30
-60
-90
-130
-170
-210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6.9747
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4.2349
3.8563
1.5521
1.3025
1.2062
1.1837
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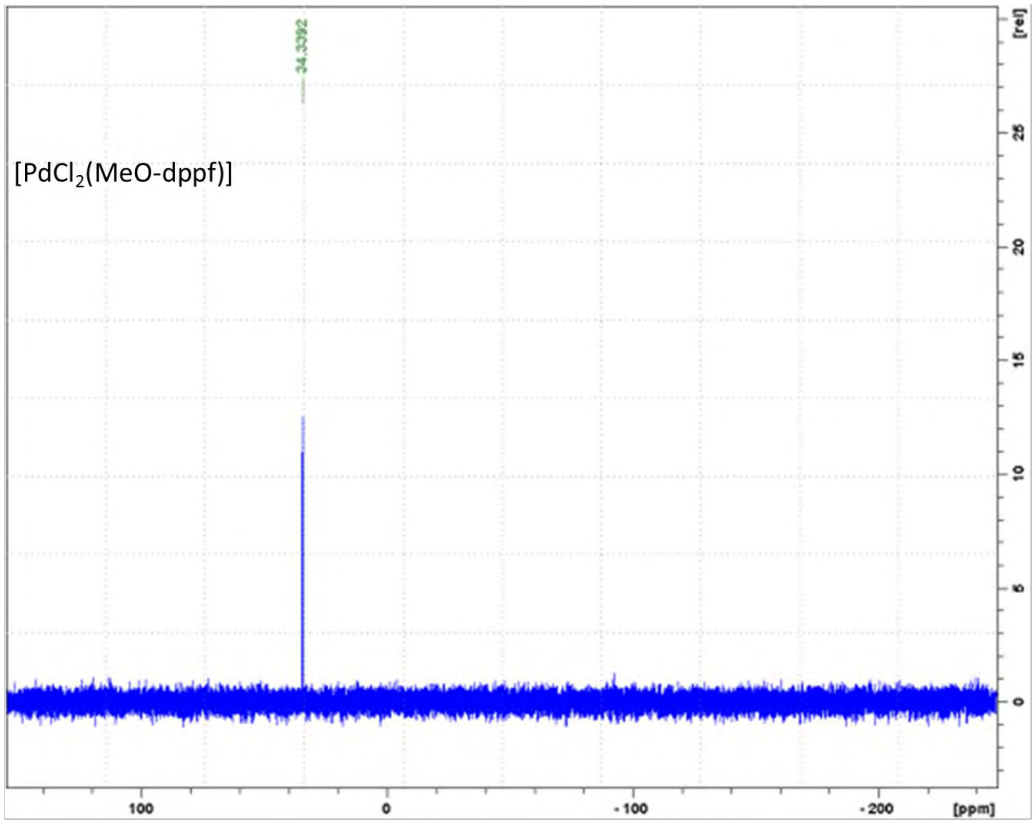
[rel]
[ppm]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[ppm]

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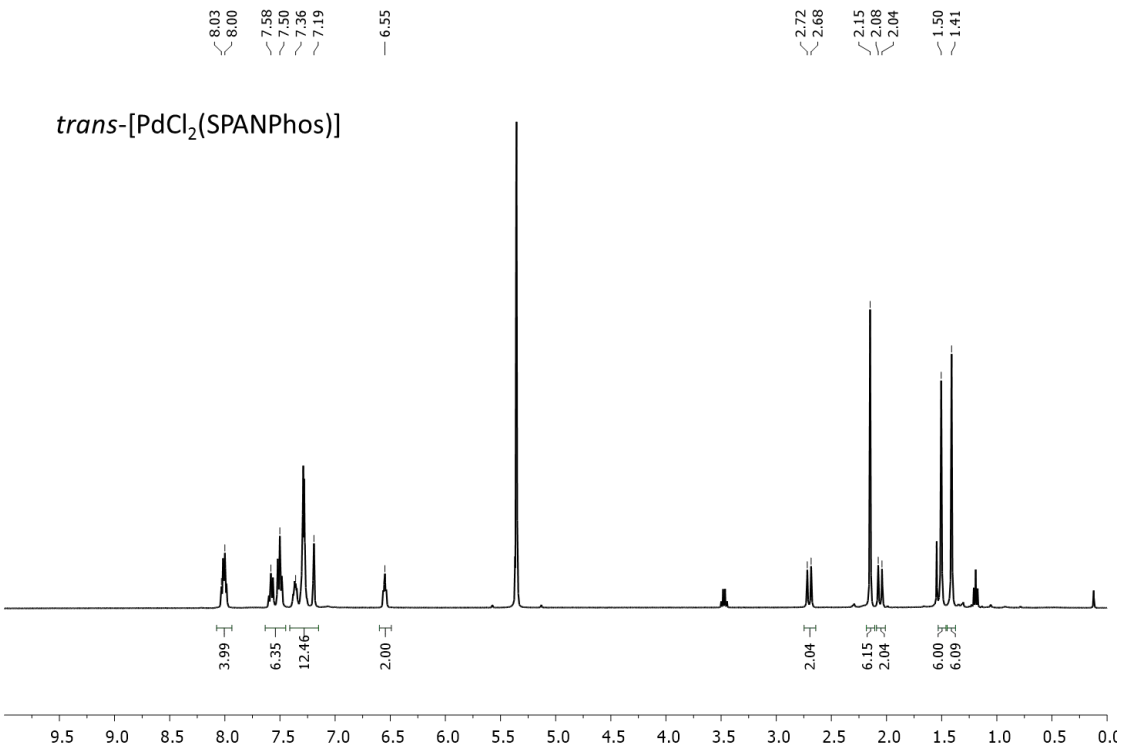
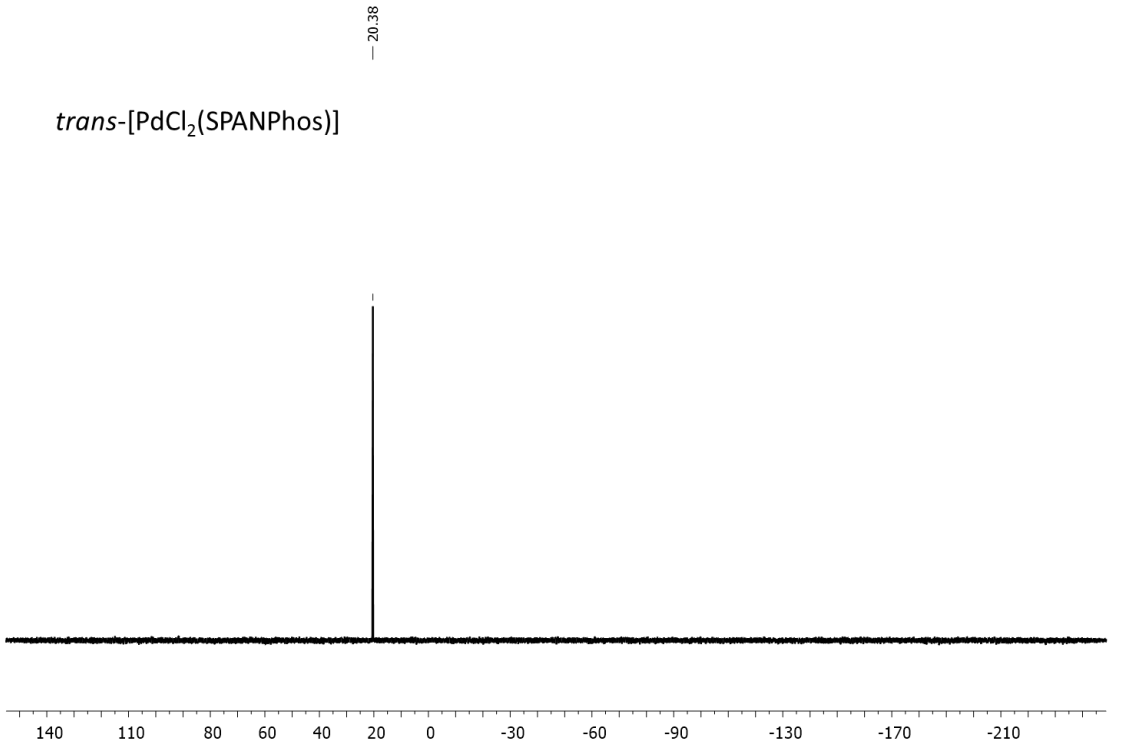
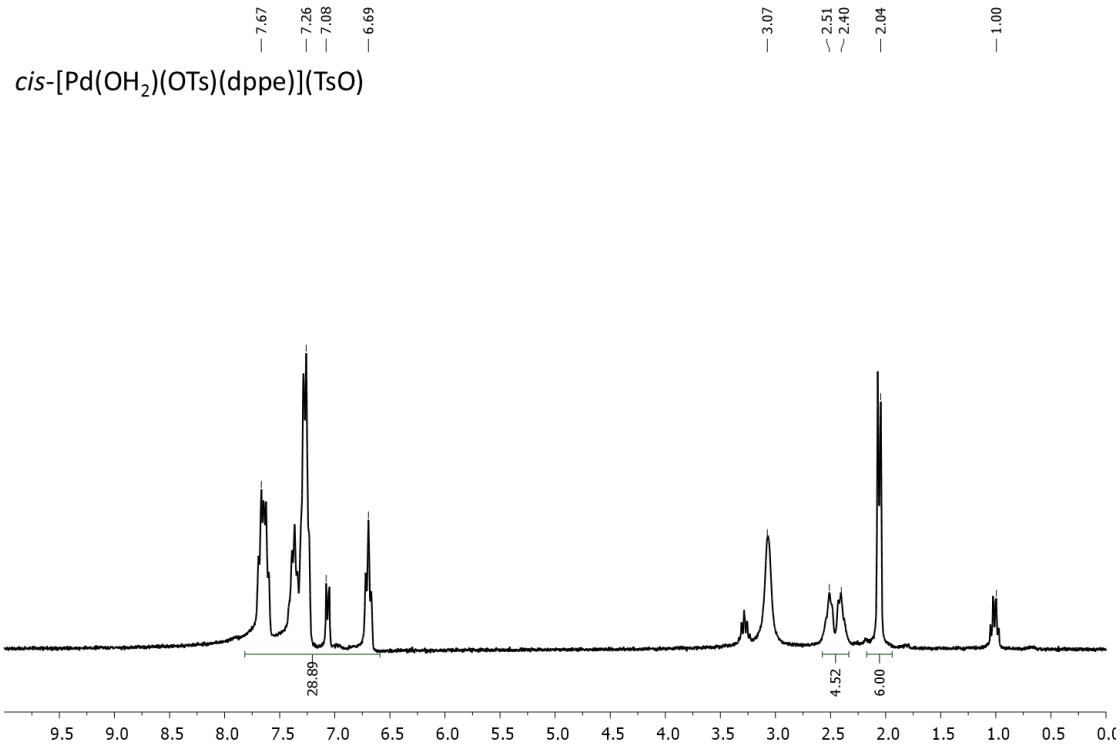


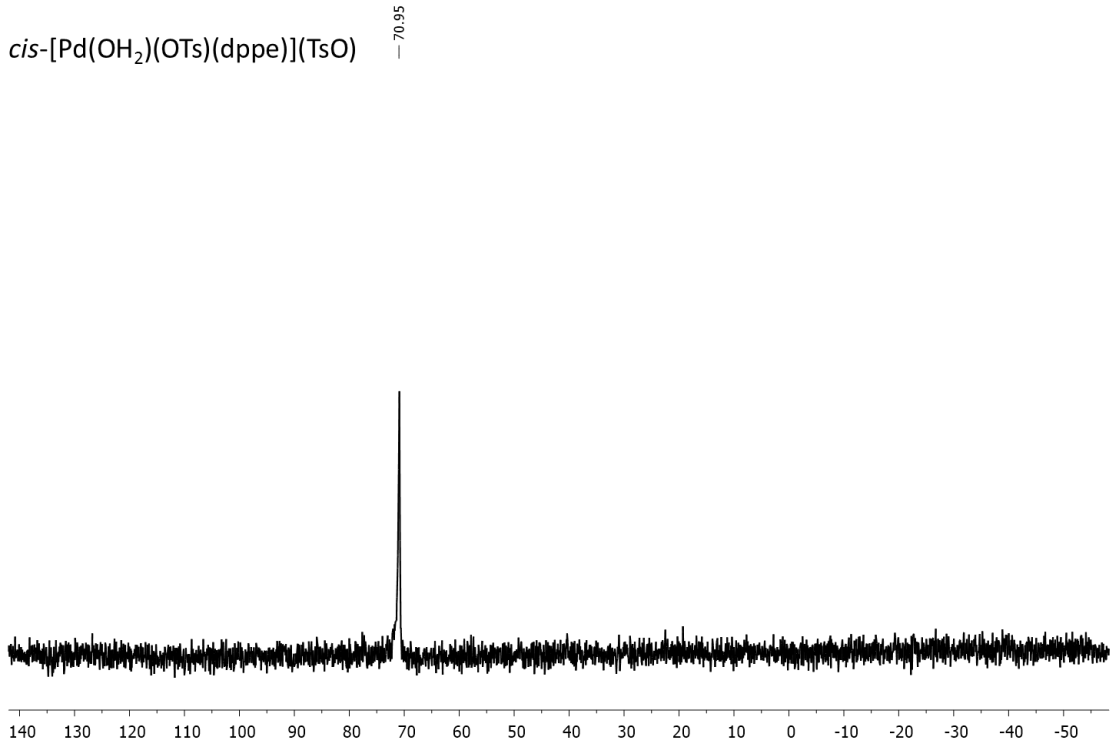
trans-[$PdCl_2$(SPANPhos)]



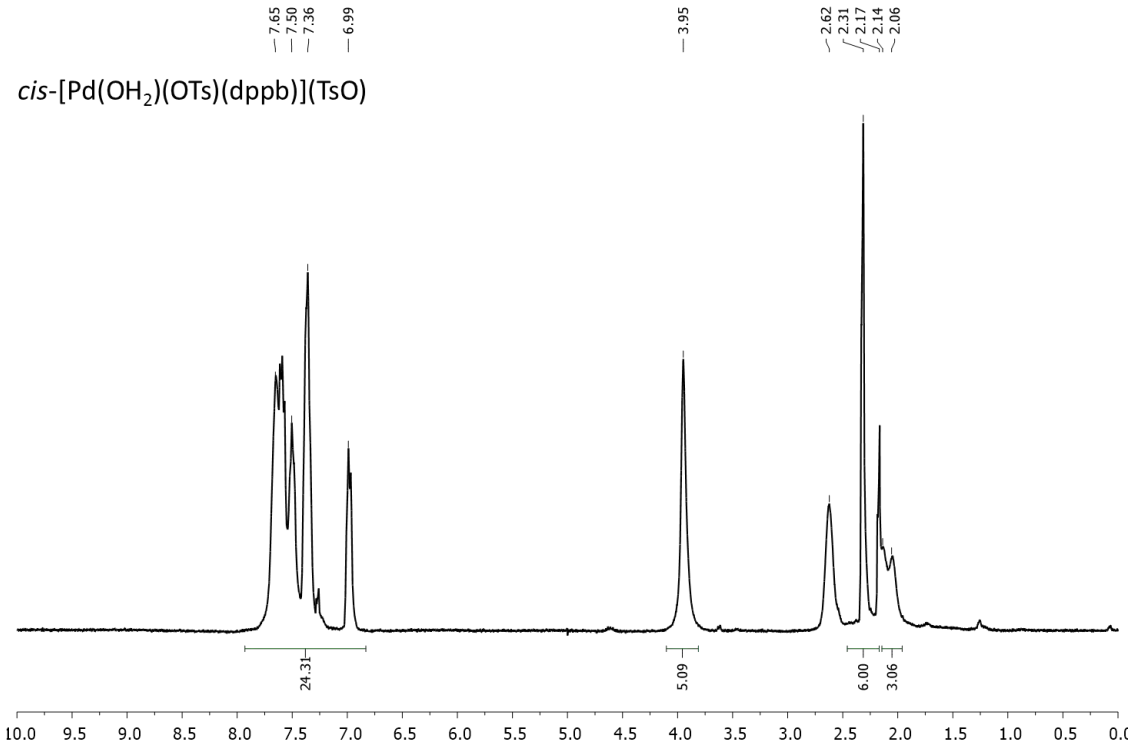
cis-[Pd(OH$_2$)(OTs)(dppe)](TsO)



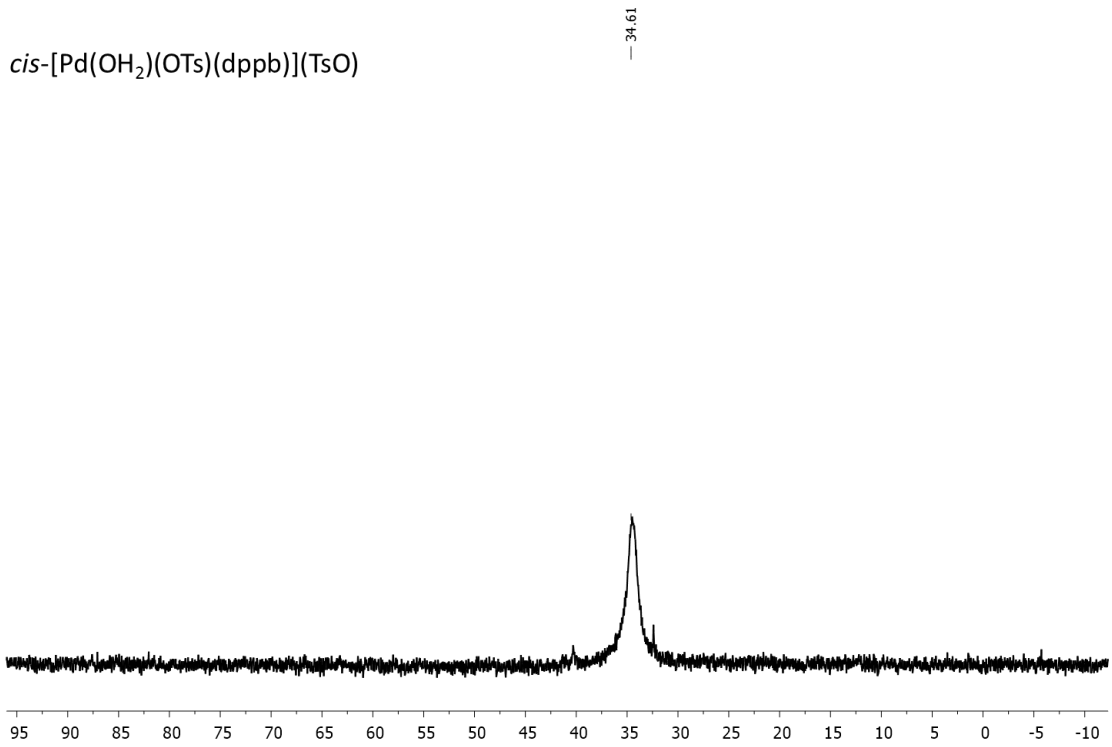
cis-[Pd(OH$_2$)(OTs)(dppe)](TsO)

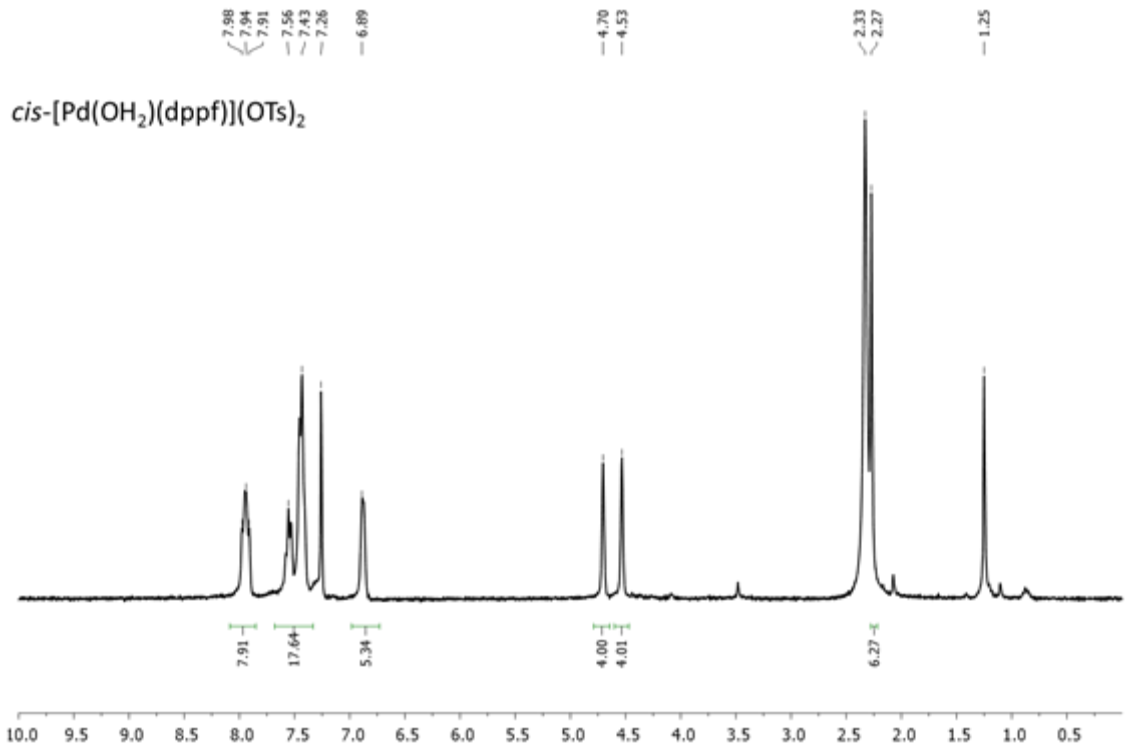


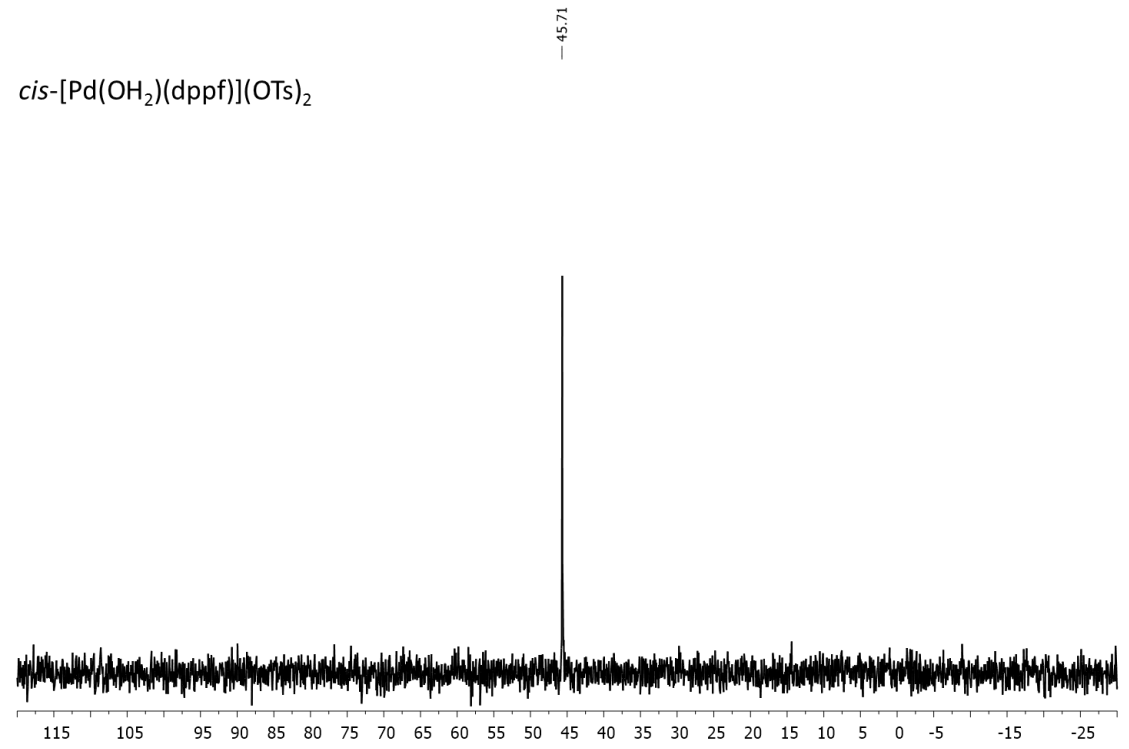
cis-[Pd(OH$_2$)(OTs)(dppb)](TsO)

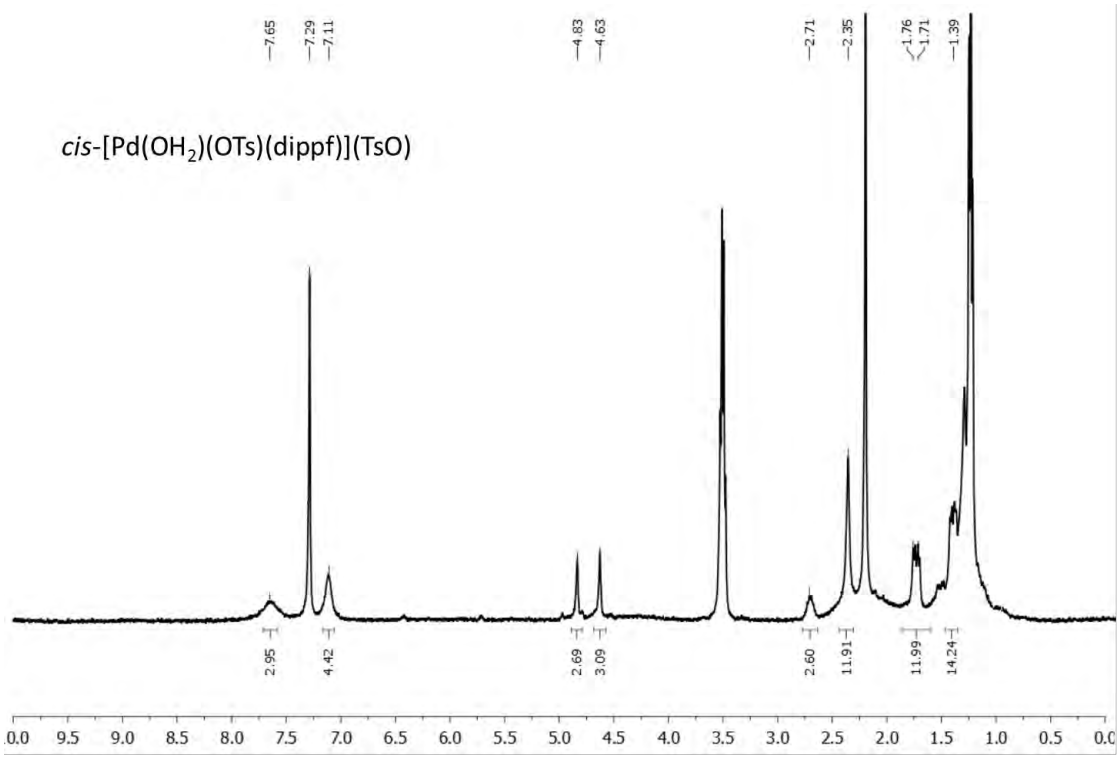


cis-[Pd(OH$_2$)(OTs)(dppb)](TsO)

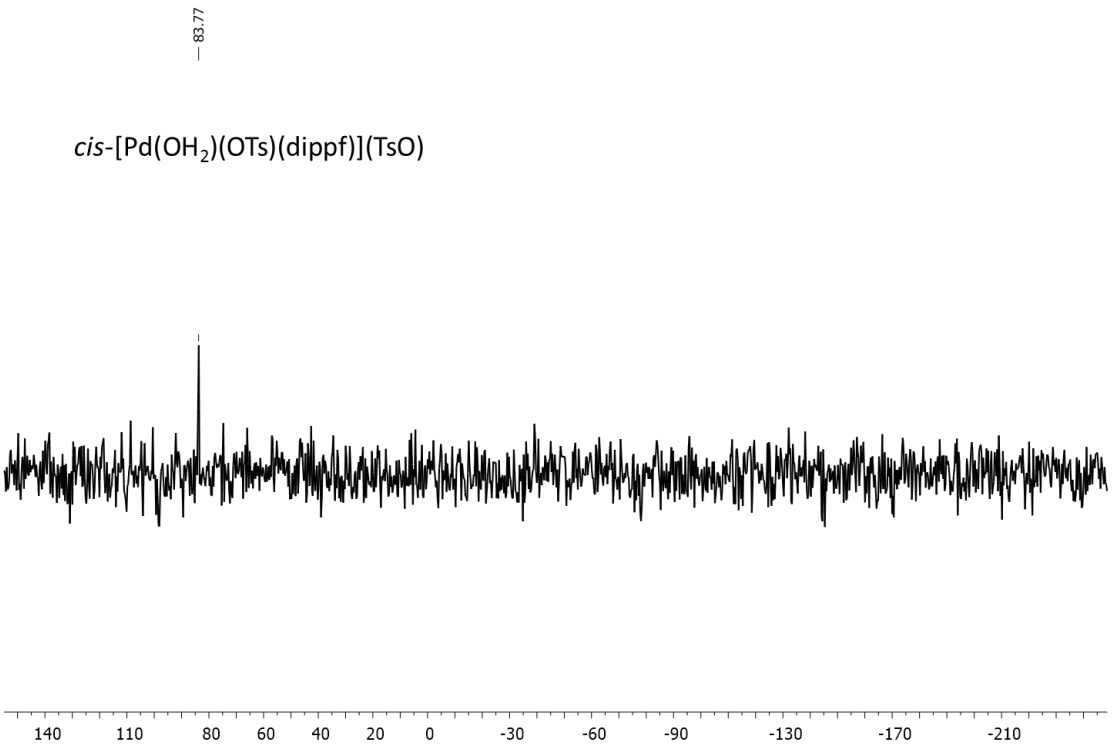


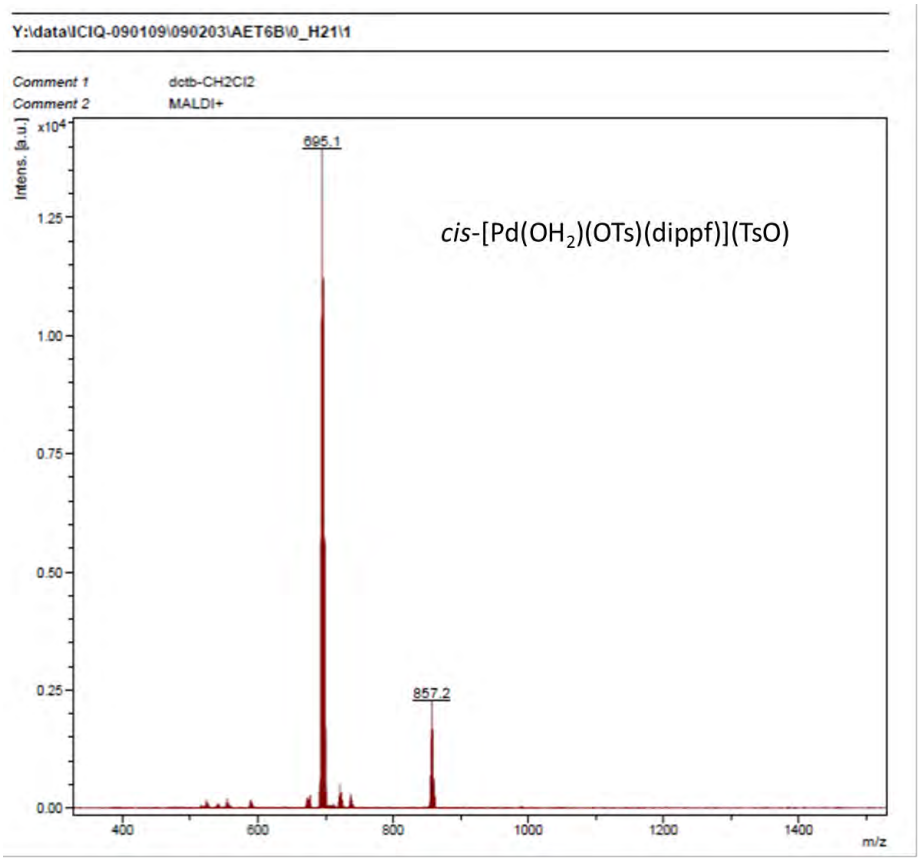

7.98
7.94
7.91
7.56
7.43
7.26
6.89
4.70
4.53
2.33
2.27
1.25
cis-[Pd(OH2)(dppf)](OTs)2
7.91
17.64
5.34
4.00
4.01
6.27
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5

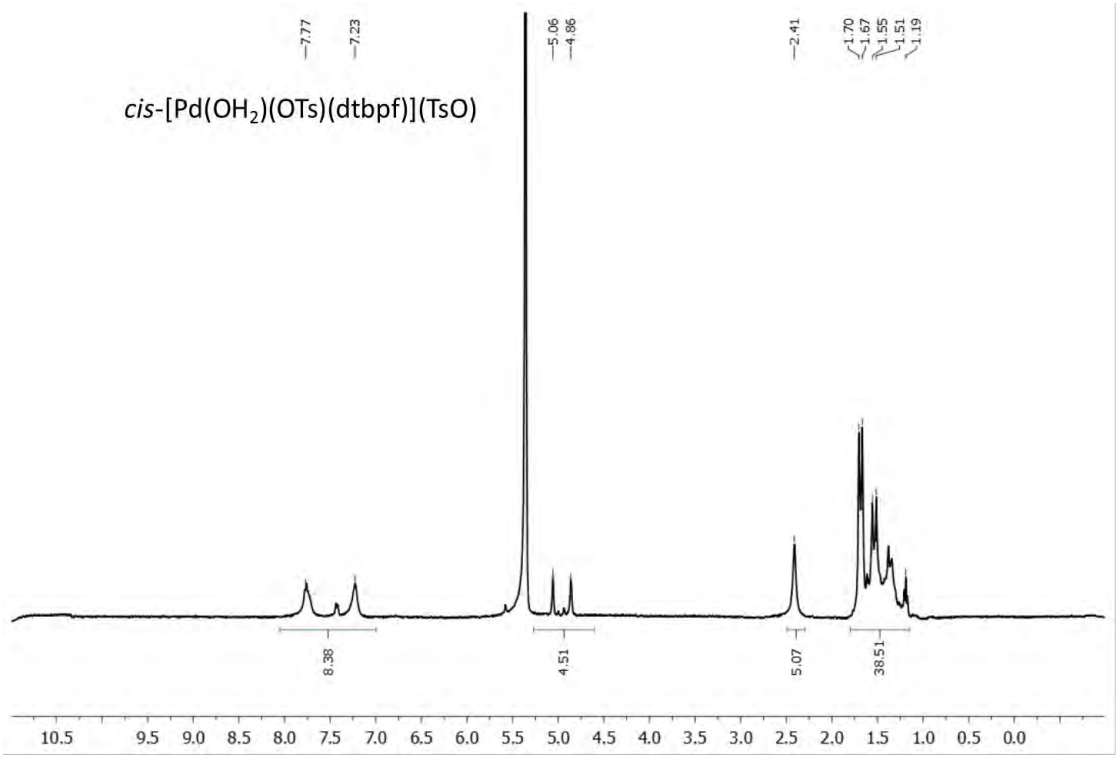

45.71
cis-[Pd(OH2)(dppf)](OTs)2
115 105 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -15 -25

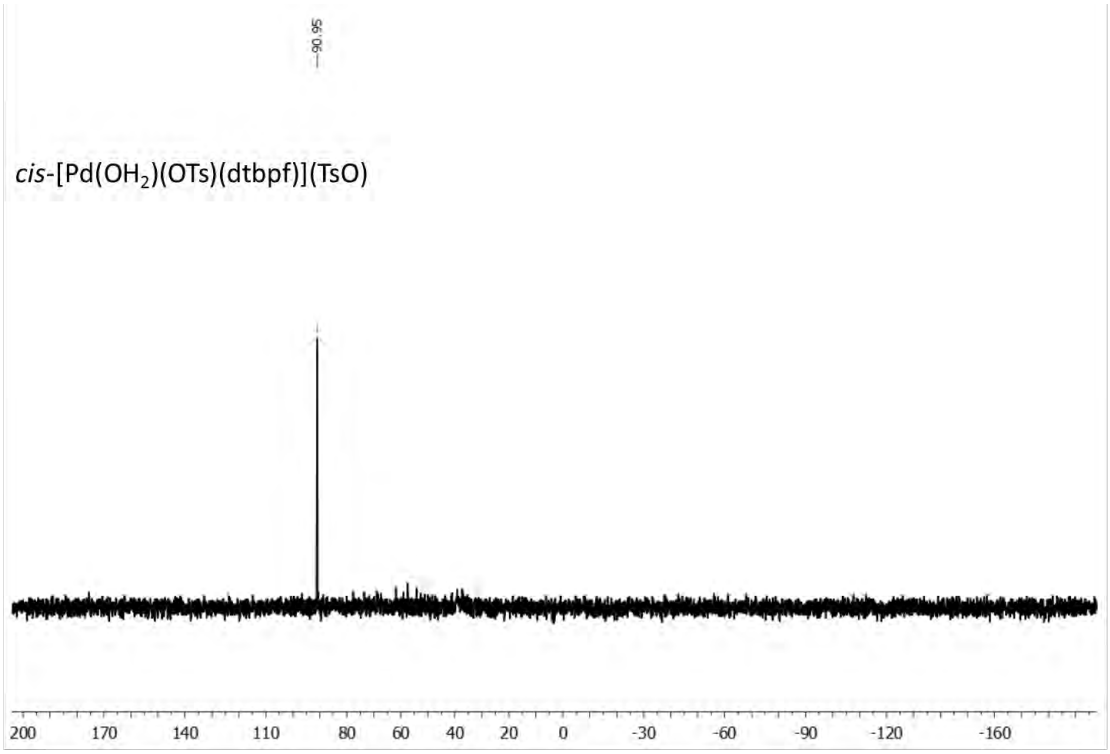


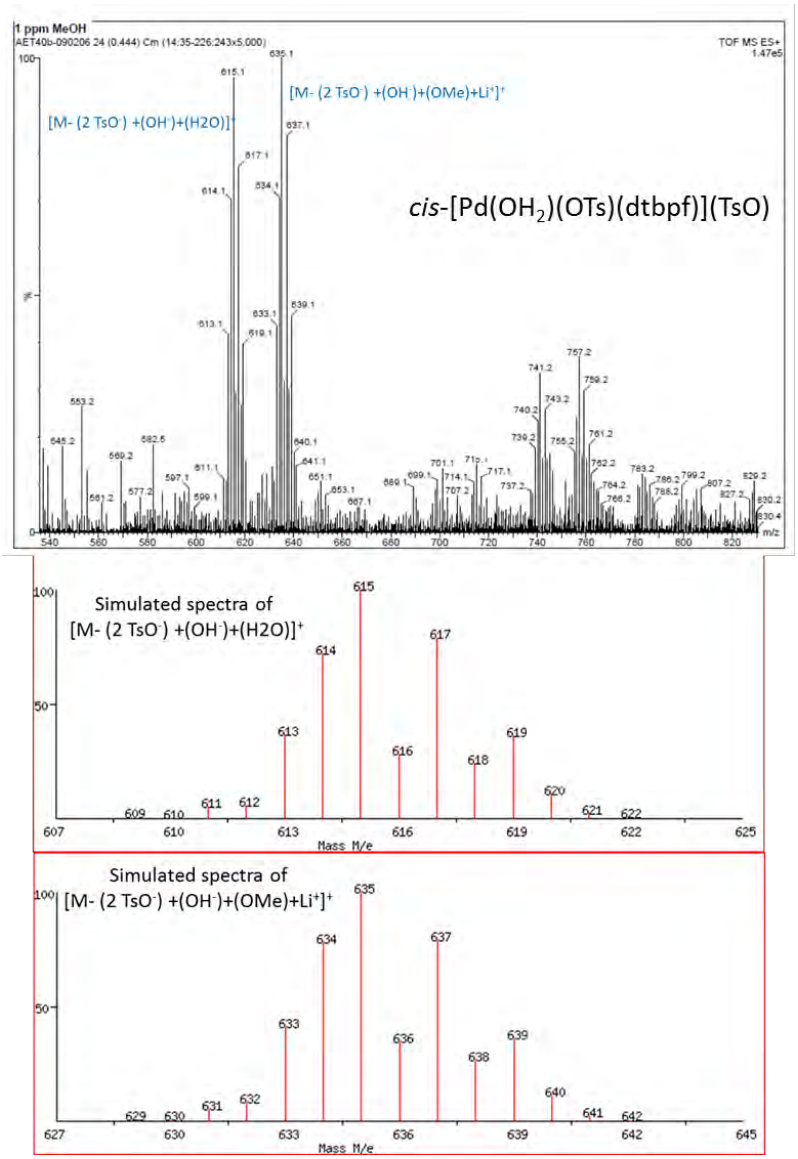
cis-[Pd(OH$_2$)(OTs)(dippf)](TsO)

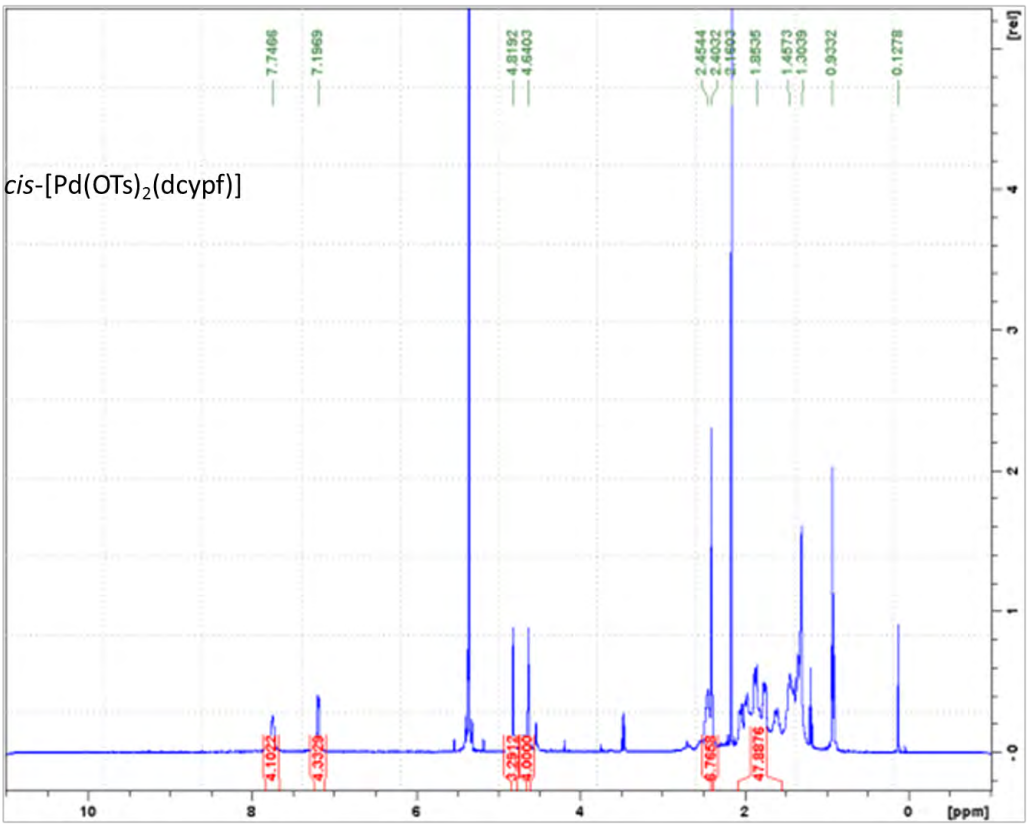


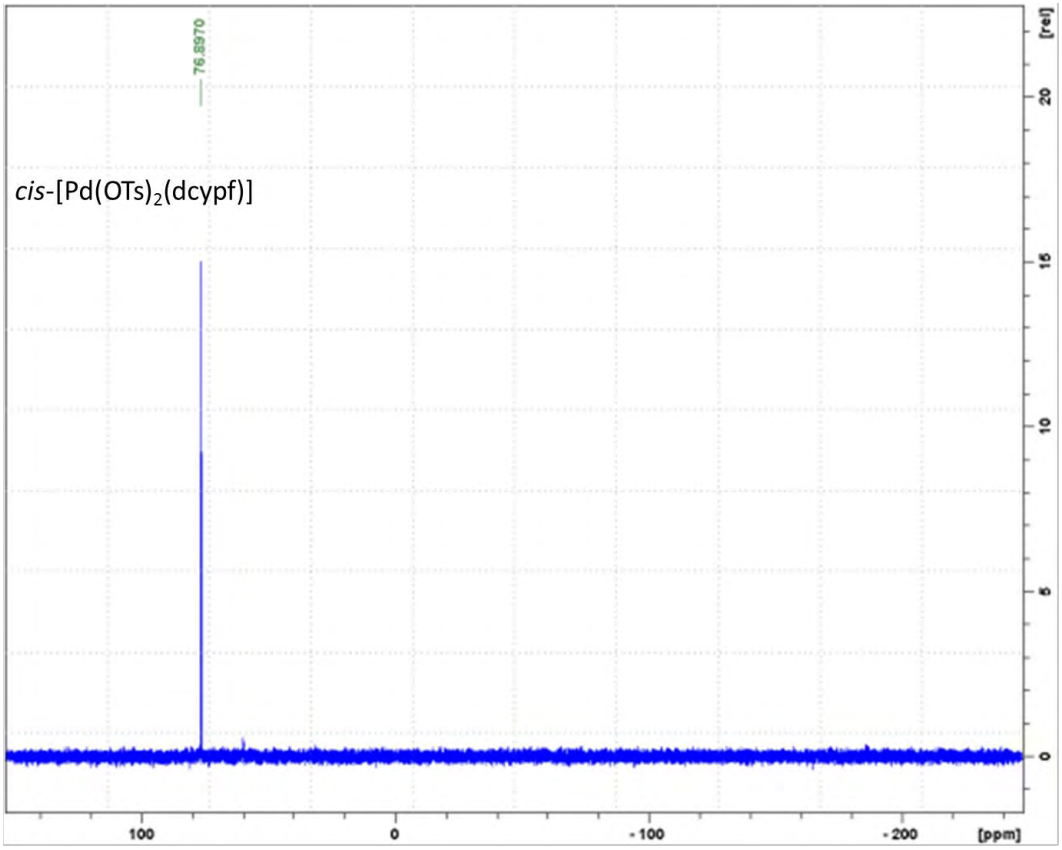

Y:\data\ICIQ-090109\090203\AET6B\0_H21\1
Comment 1
dctb-CH2Cl2
Comment 2
MALDI+
Intens. [a.u.]
x10^4
695.1
857.2
m/z
cis-[Pd(OH2)(OTs)(dippf)](TsO)

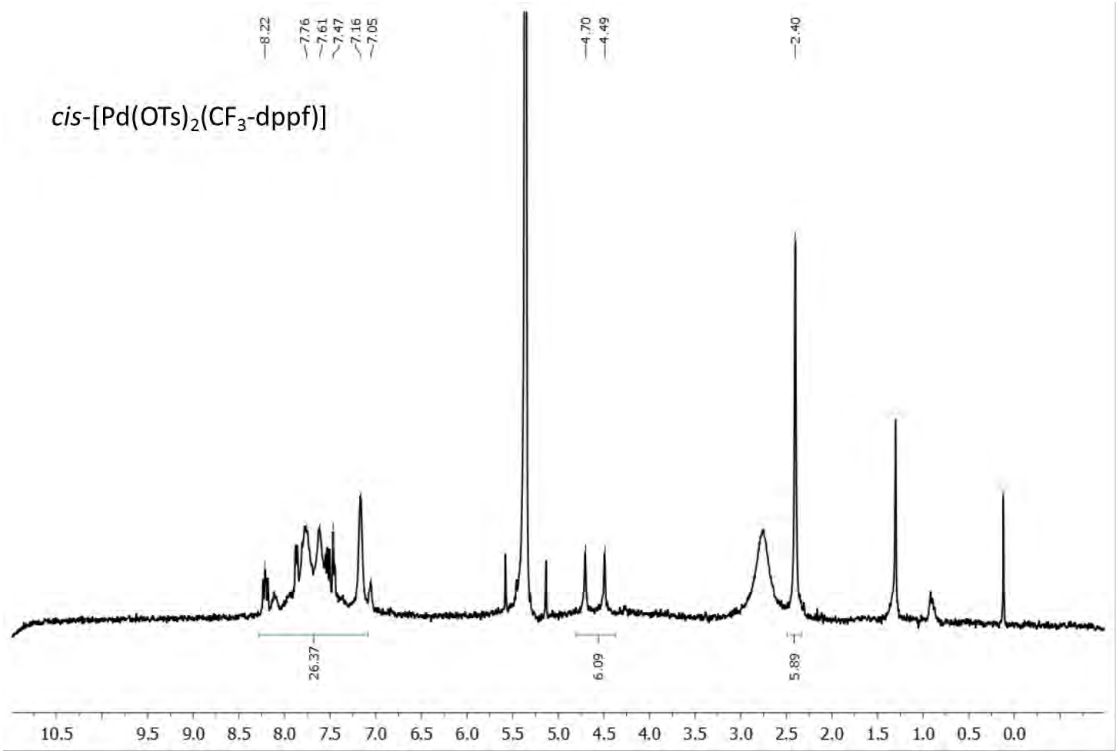

cis-[Pd(OH2)(OTs)(dtbpf)](TsO)
7.77
7.23
5.06
4.86
2.41
1.70
1.67
1.55
1.51
1.19
8.38
4.51
5.07
38.51

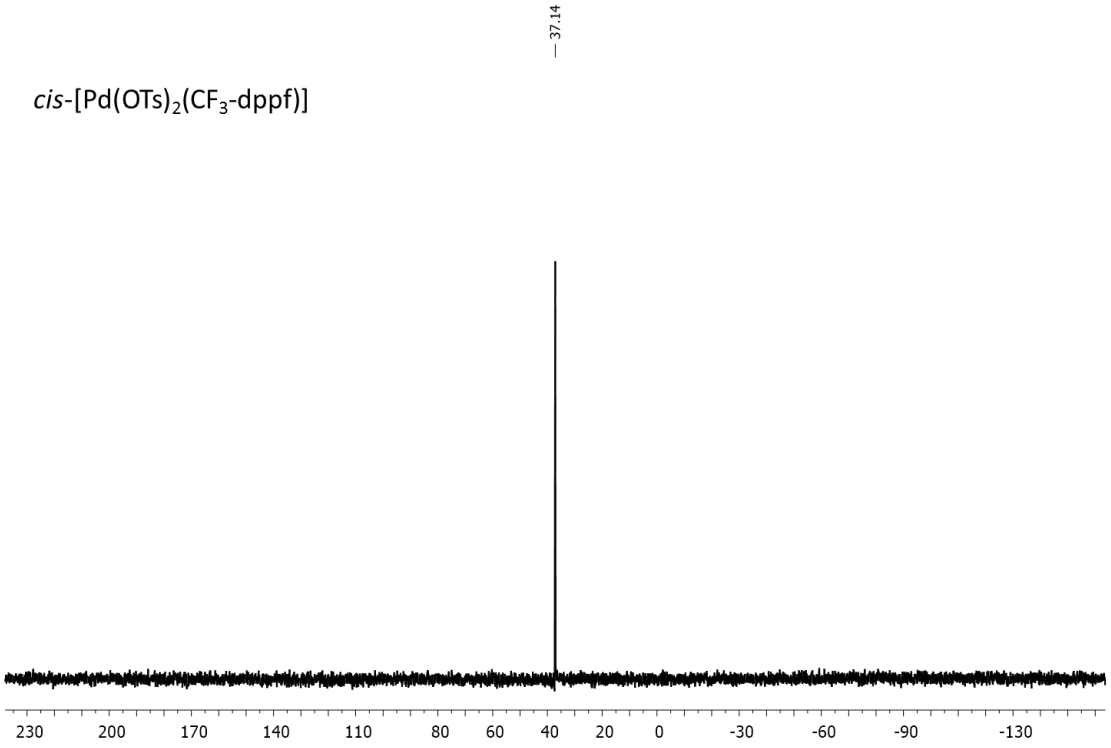

90.95
cis-[Pd(OH2)(OTs)(dtbpf)](TsO)
200
170
140
110
80
60
40
20
0
-30
-60
-90
-120
-160

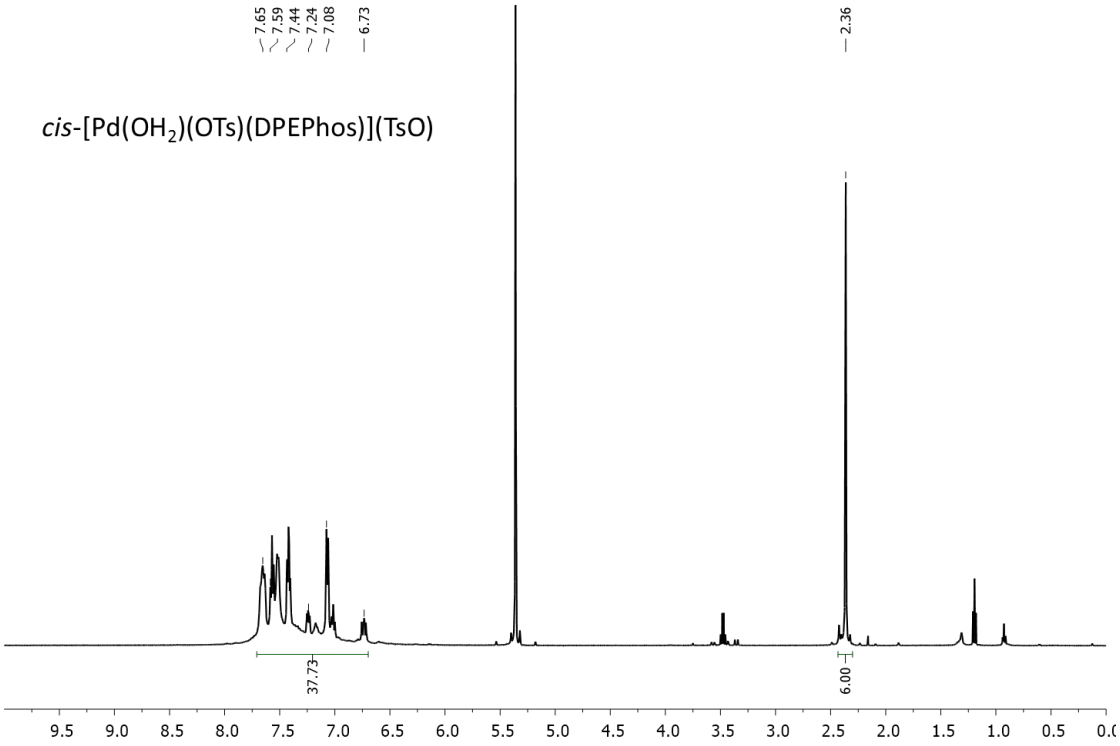

1 ppm MeOH
TOF MS ES+
1.47e5
[M- (2 TsO-) +(OH-)+(H2O)]+
[M- (2 TsO-) +(OH-)+(OMe)+Li+]+
cis-[Pd(OH2)(OTs)(dtbpf)](TsO)
Simulated spectra of
[M- (2 TsO-) +(OH-)+(H2O)]+
Mass M/e
Simulated spectra of
[M- (2 TsO-) +(OH-)+(OMe)+Li+]+
Mass M/e


cis-[Pd(OTs)2(dcypf)]
7.7466
7.1969
4.8192
4.6403
2.4544
2.4032
2.1603
1.8535
1.4573
1.3039
0.9332
0.1278
4.1022
4.3529
2.2815
4.0000
6.7668
47.8876
10
8
6
4
2
0
[ppm]
[rel]

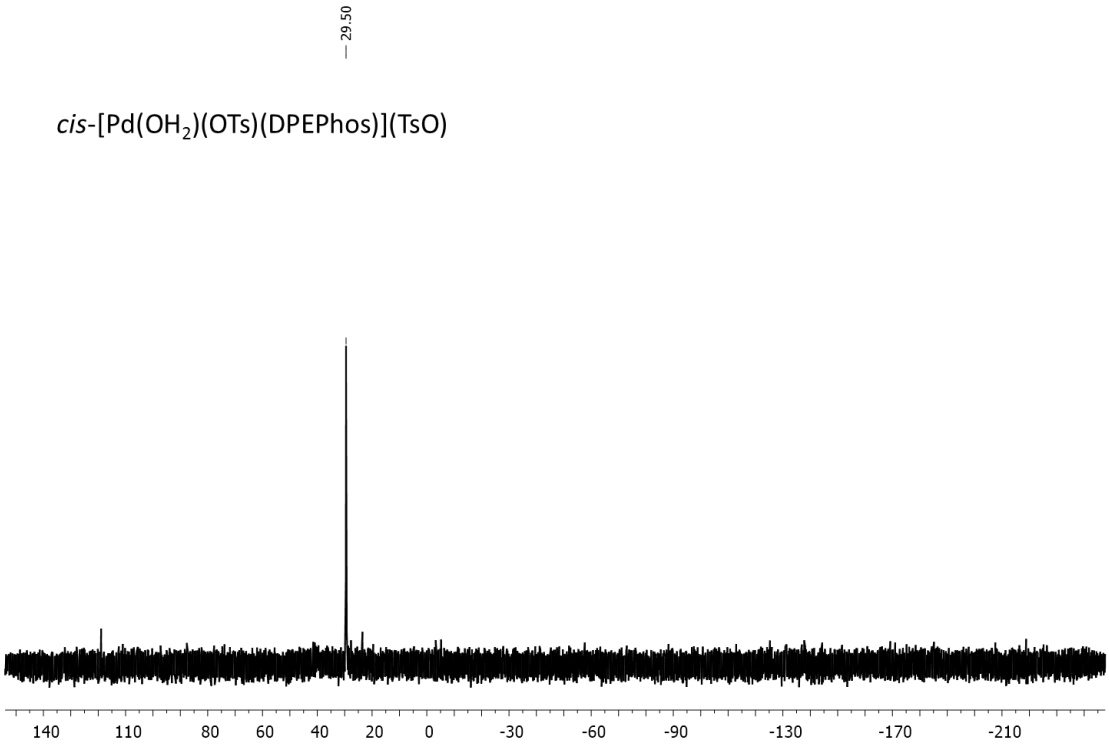

cis-[Pd(OTs)2(dcypf)]
76.8970
100
0
-100
-200
[ppm]
[rel]


8.22
7.76
7.61
7.47
7.16
7.05
4.70
4.49
2.40
cis-[Pd(OTs)2(CF3-dppf)]
26.37
6.09
5.89
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

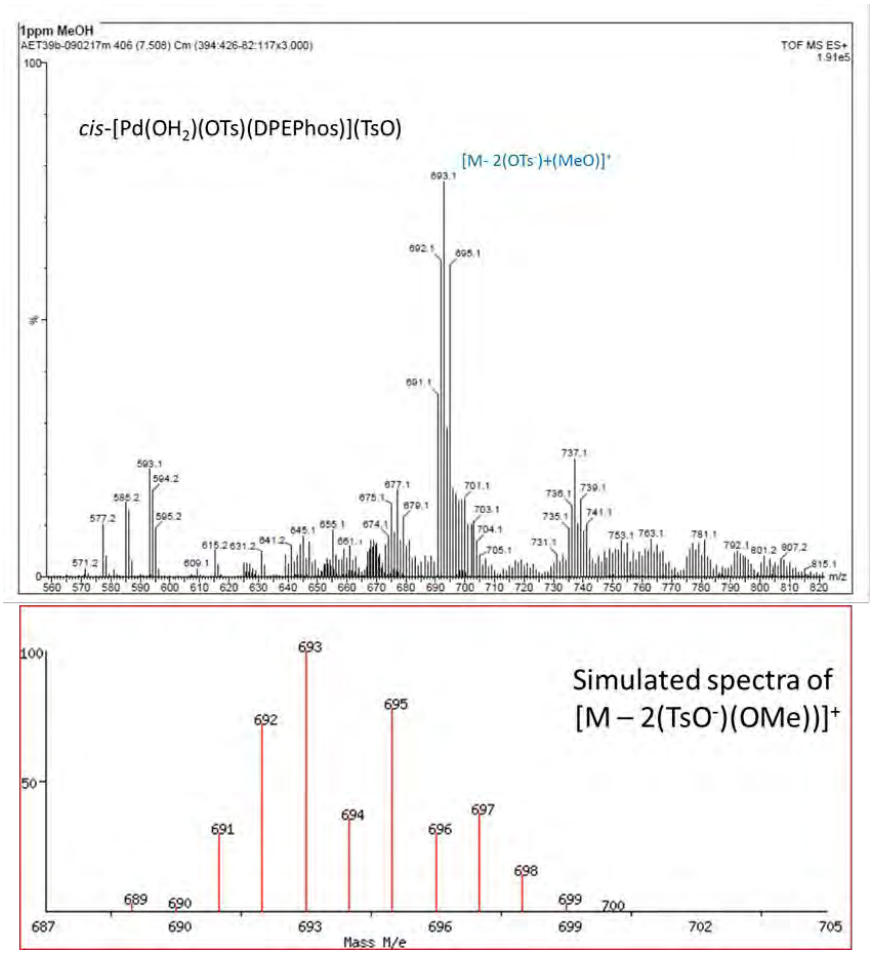

37.14
cis-[Pd(OTs)2(CF3-dppf)]
230 200 170 140 110 80 60 40 20 0 -30 -60 -90 -130



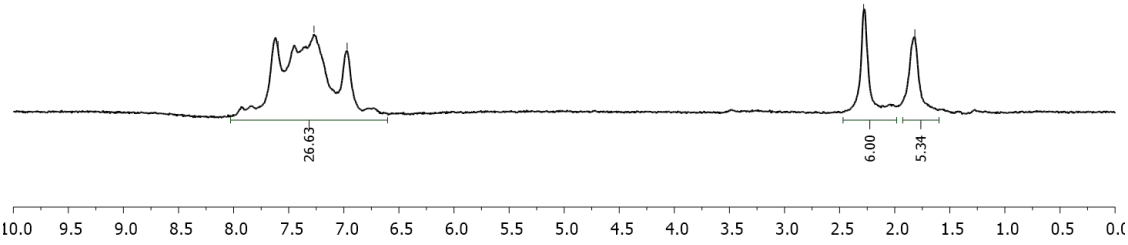
cis-[Pd(OH$_2$)(OTs)(DPEPhos)](TsO)



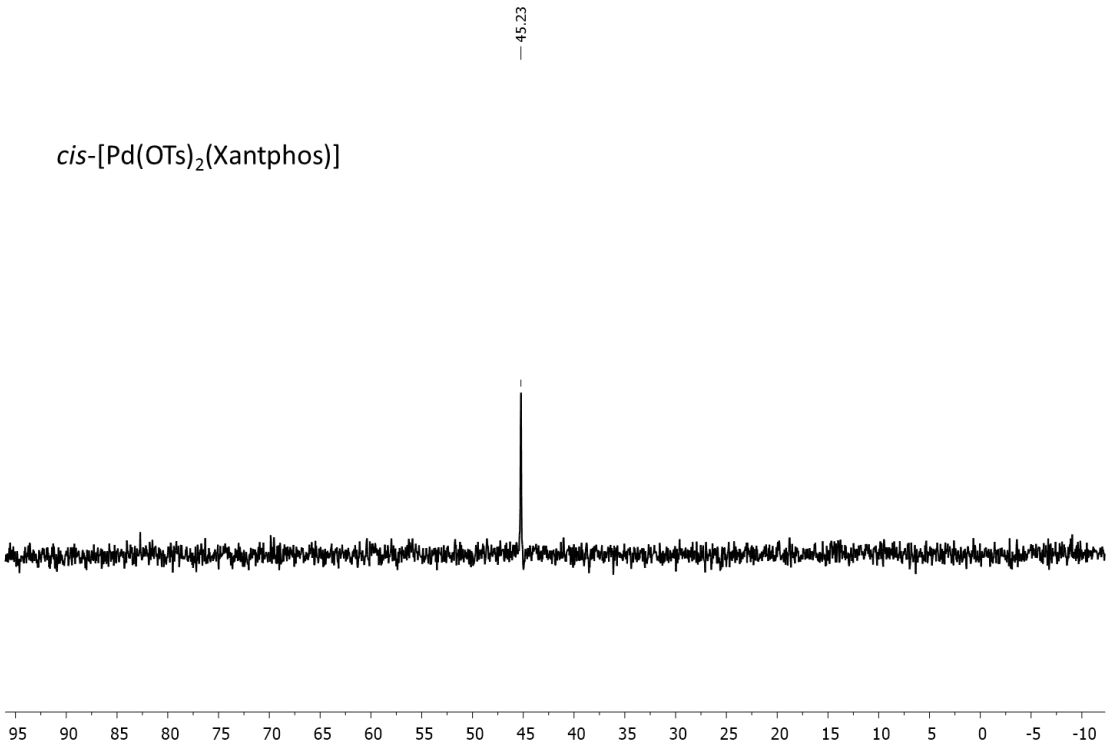
cis-[Pd(OH$_2$)(OTs)(DPEPhos)](TsO)



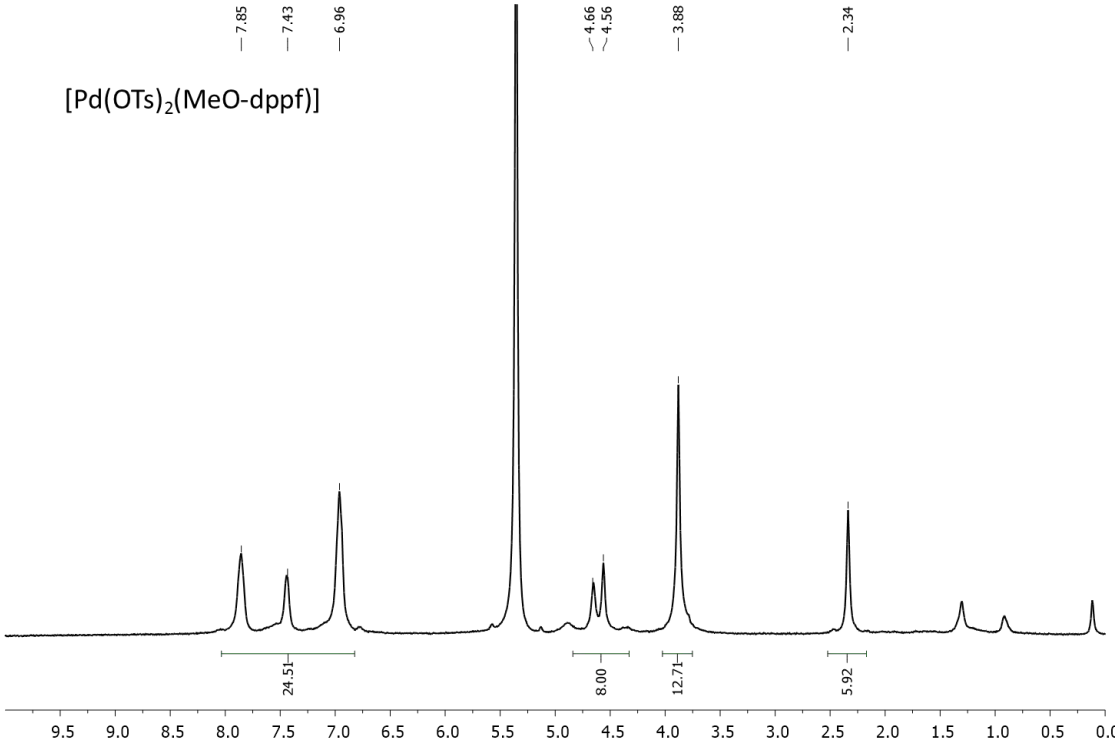
cis-[Pd(OTs)$_2$(Xantphos)]



cis-[Pd(OTs)$_2$(Xantphos)]

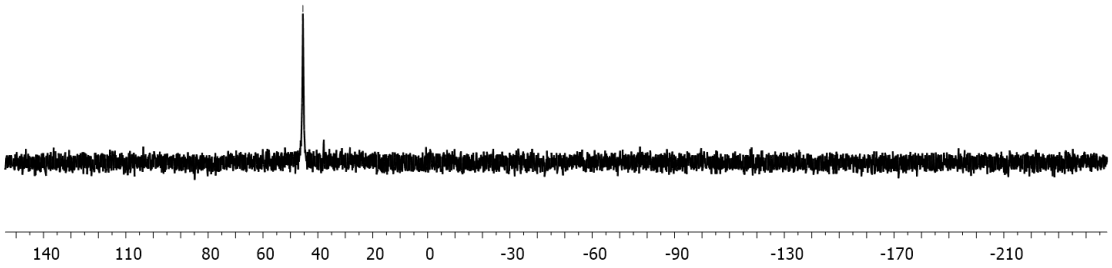


[Pd(OTs)$_2$(MeO-dppf)]

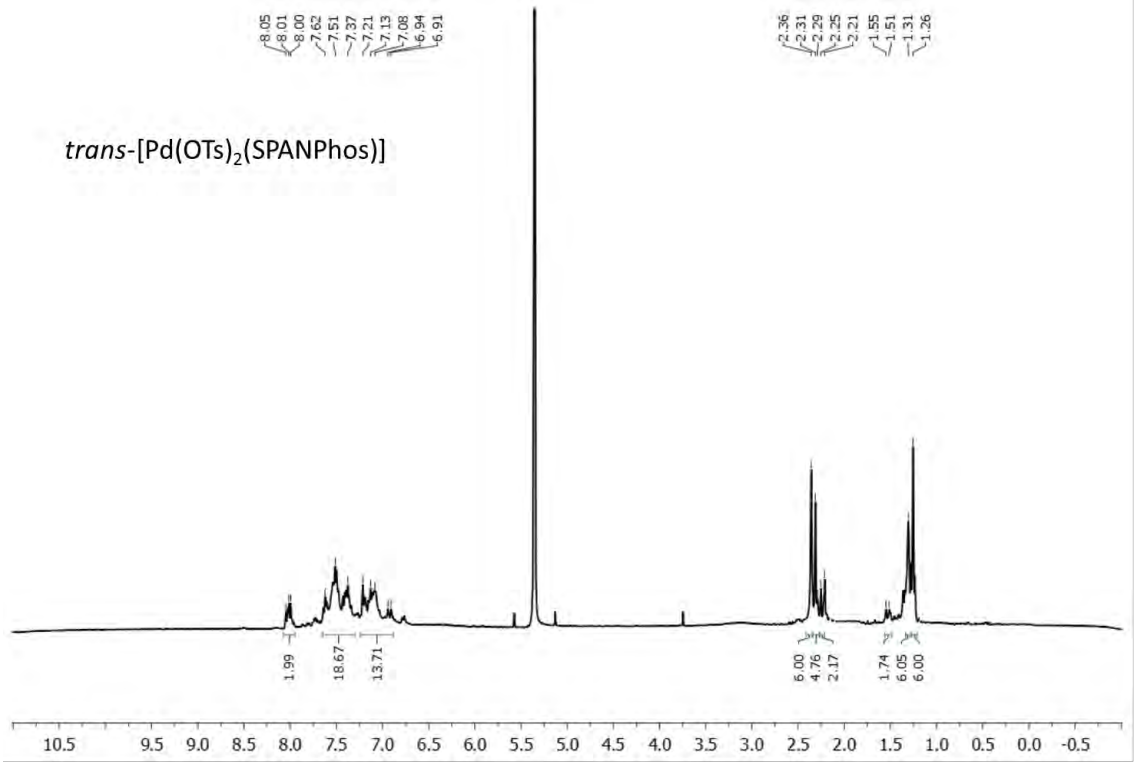


45.44

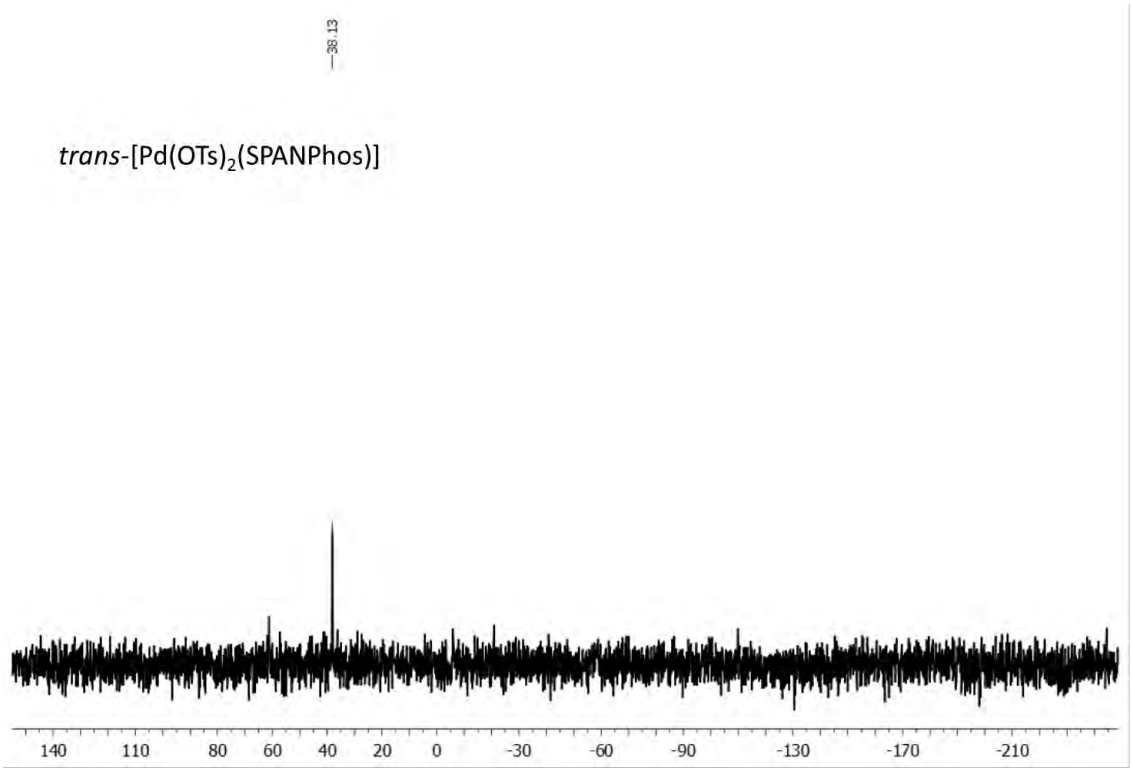
[Pd(OTs)$_2$(MeO-dppf)]



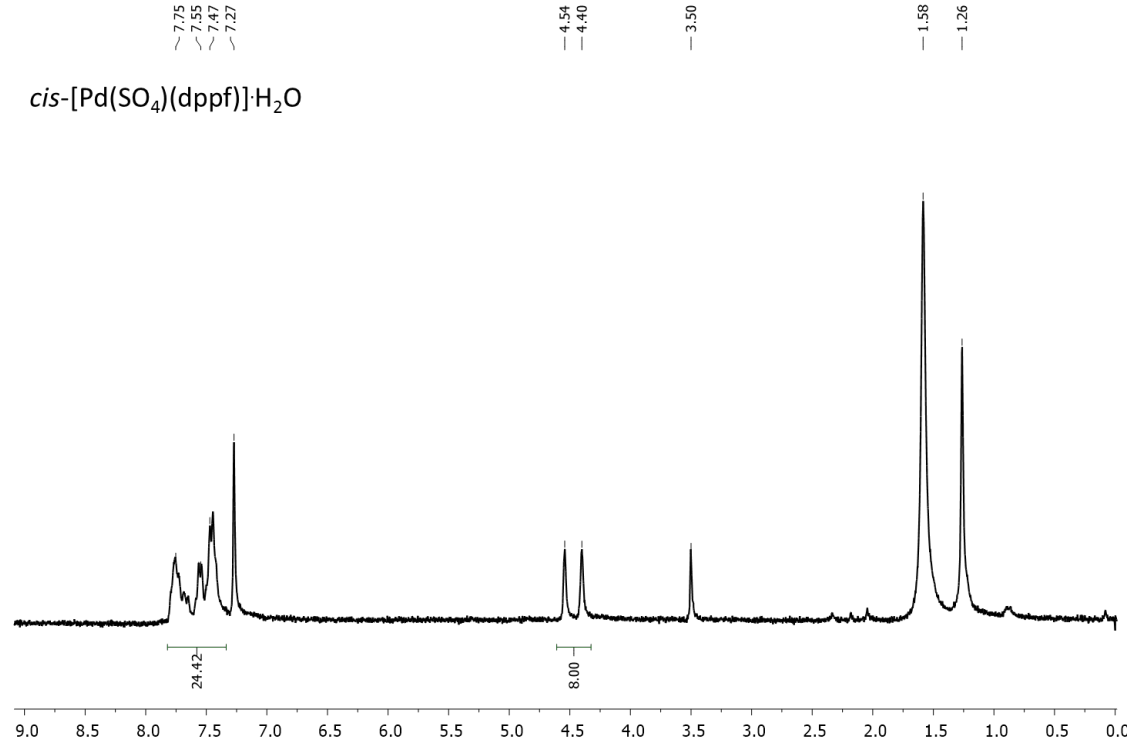
trans-[Pd(OTs)$_2$(SPANPhos)]



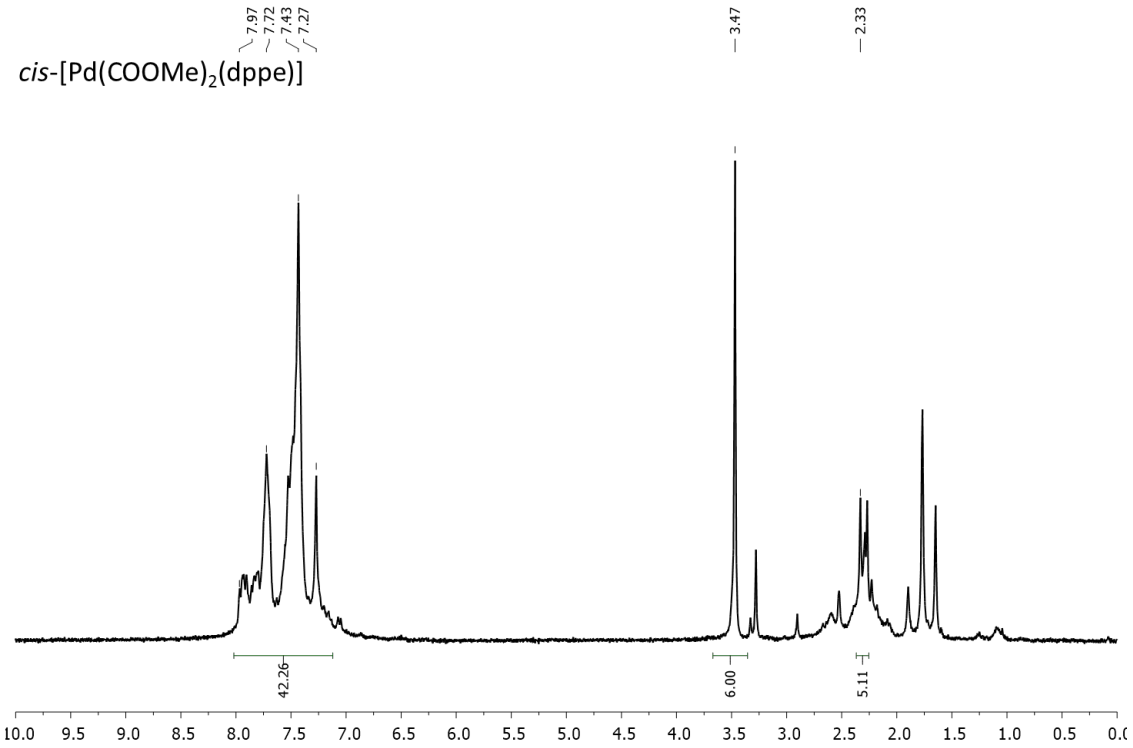
trans-[Pd(OTs)$_2$(SPANPhos)]



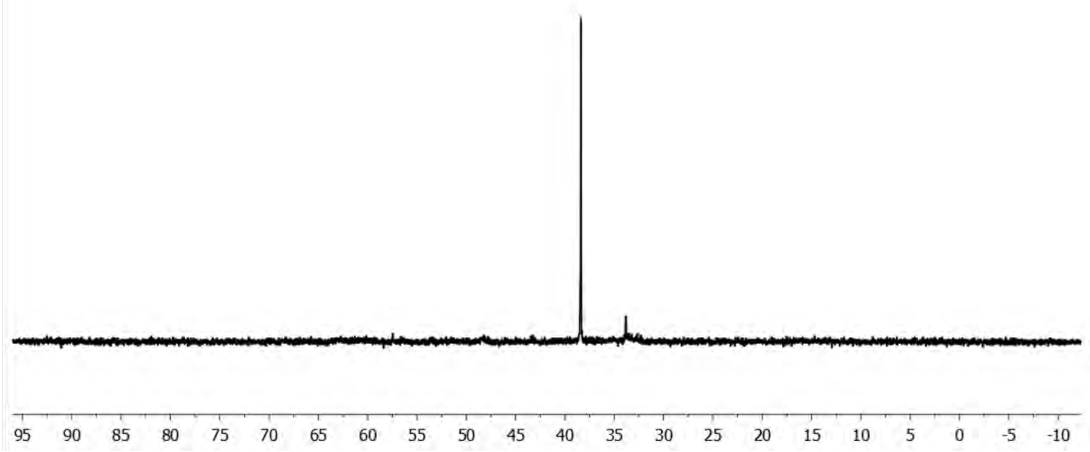
cis-[Pd(SO$_4$)(dppf)]·H$_2$O



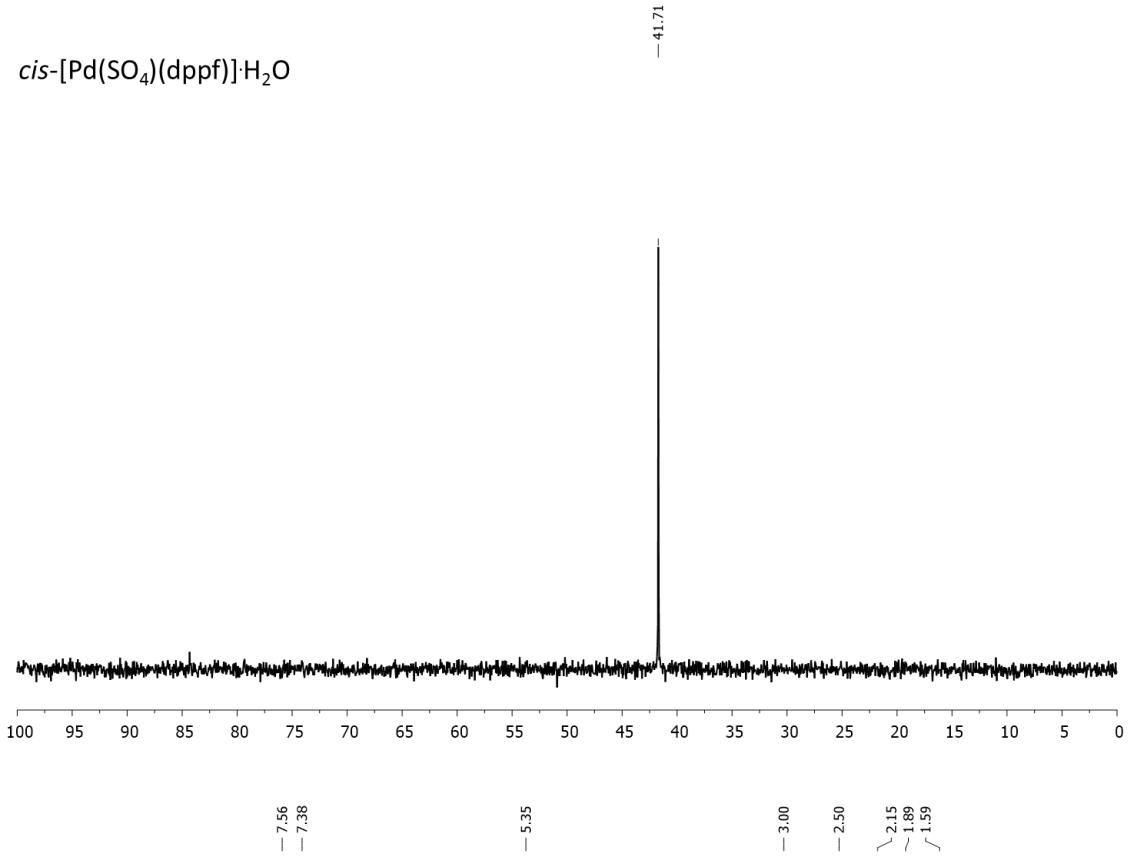
cis-[Pd(COOMe)$_2$(dppe)]



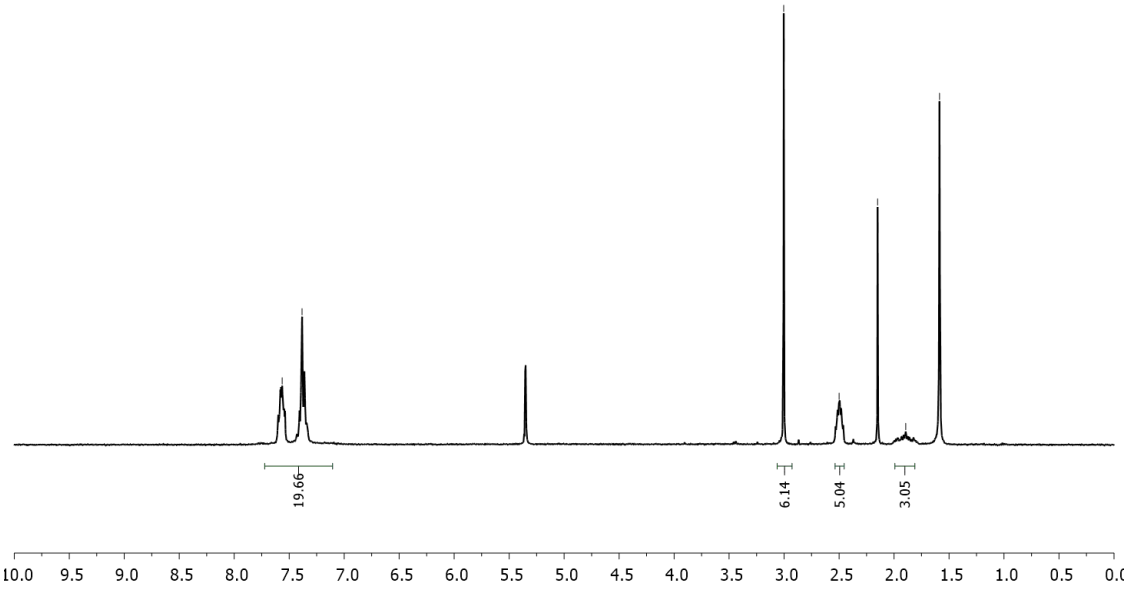
cis-[Pd(COOMe)$_2$(dppe)]



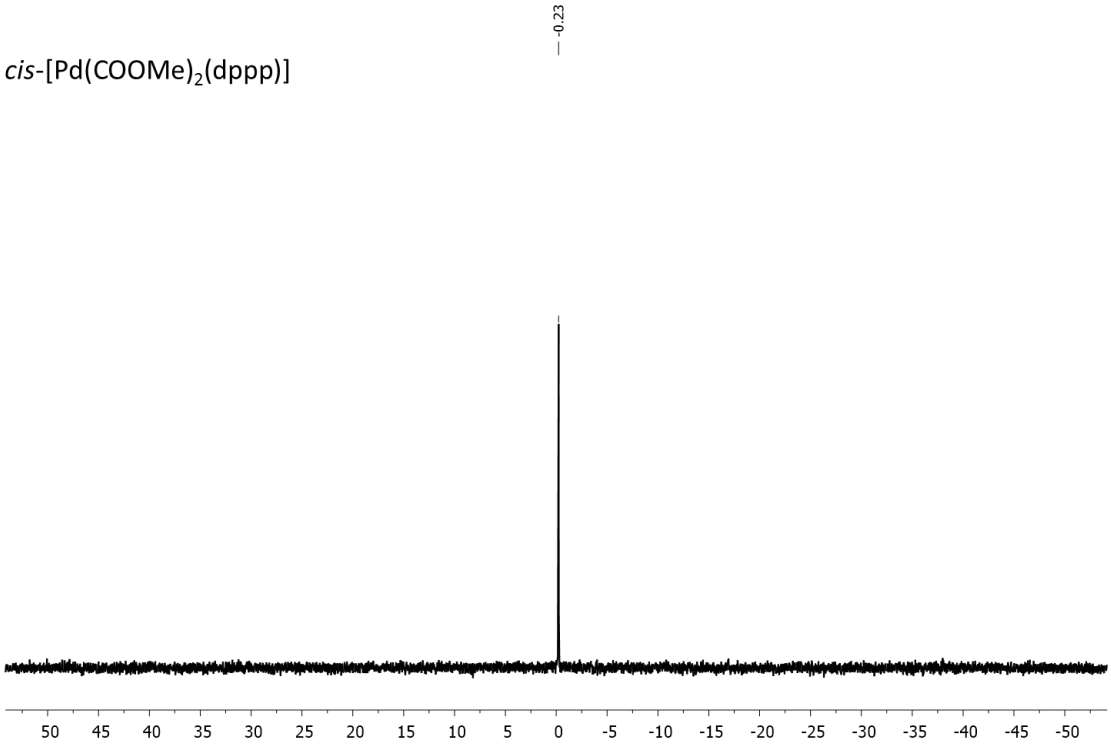
cis-[Pd(SO_4)(dppf)]·H_2O



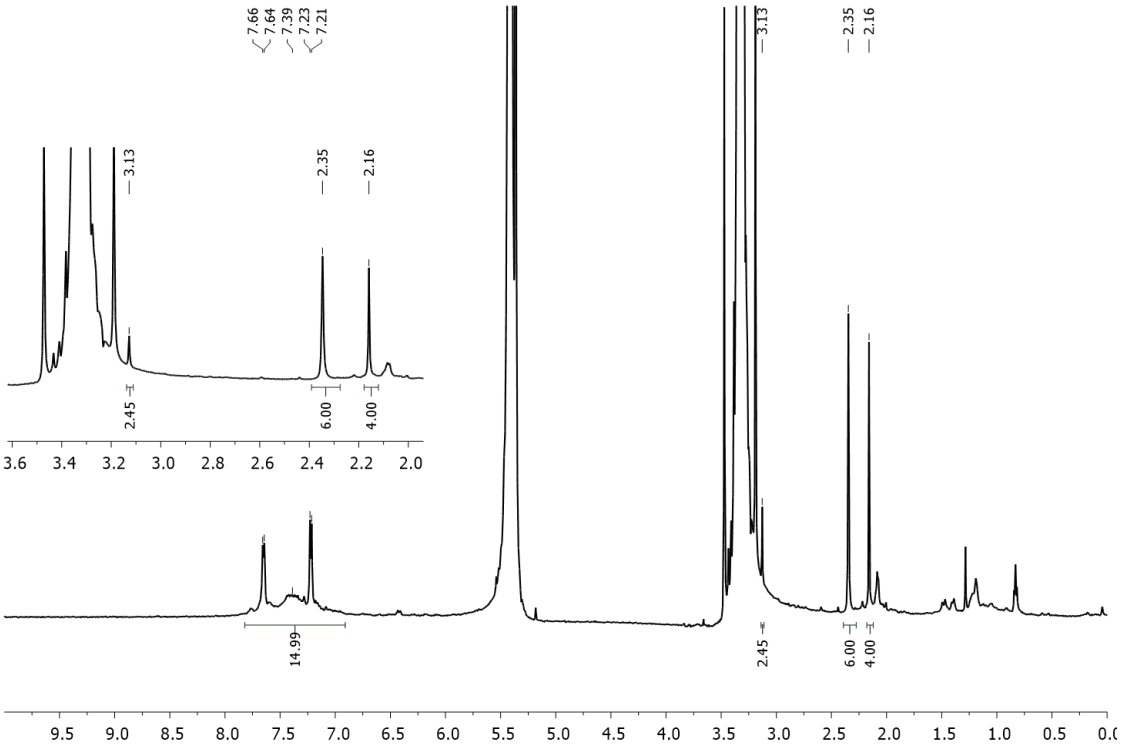
cis-[Pd($COOMe)_2$(dppp)]



cis-[Pd(COOMe)$_2$(dppp)]



trans-[Pd(COOMe)(OTs)(SPANPhos)] · TsOH



trans-[Pd(COOMe)(OTs)(SPANPhos)] · TsOH