(In situ) spectroscopic studies on state-of-the-art Pd(II) catalysts in solution for the alkoxycarbonylation of alkenes

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Supporting Information -Table of Contents

SI-A: General remarks on NMR spectroscopic measurements

NMR spectra were recorded at Bruker spectrometers (Avance III HD 300 and 400) at ambient temperature (297-298 K), unless stated otherwise.[1,2] Chemical shifts are given on the δ scale and are referenced by means of the solvent signals (^{1}H, ^{13}C) or calculated reference frequencies ($\varXi$ convention). The following values were used: [1]H, methanol-d_4 3.32 ppm, dichloromethane-d_2 5.32 ppm; ^{13}C, methanol-d_4 49.0 ppm, dichloromethane-d_2 53.8 ppm; ^{15}N, $\varXi$ = 10.136 767 MHz (which corresponds to neat nitromethane at 0 ppm); ^{19}F, $\varXi$ = 94.094 011 MHz (which corresponds to CCl_3F at 0 ppm); ^{31}P, $\varXi$ = 40.480 742 MHz (which corresponds to 85% phosphoric acid at 0 ppm). [15]N chemical shifts were determined by inverse detection (standard HMBC sequence with gradient selection), each measurement was performed at least twice with variation of nitrogen frequency and t_1 increment to ensure that the signals were not folded. 2D exchange spectra (^{1}H and ^{31}P) were acquired by the standard three-pulse NOESY experiment, with decoupling of the second nucleus (phosphorus for ^{1}H spectra and hydrogen for ^{31}P spectra) during the entire sequence, in phase-sensitive mode.

SI-B: NMR-Characterization of the free diphosphine ligands (**L1**, **L2**, **L3**)

All preparations of solutions and transfers were carried out under argon atmosphere by using standard Schlenk techniques. Sample preparation was done by dissolving 0.03 mmol of ligand (13.1 mg **L1,** 15.5 mg **L2**, 11.8 mg **L3**,) in 0.8 mL of dry dichloromethane-d_2 and transferring the resulting solutions into J. Young-NMR tubes.

Phosphine **L1**
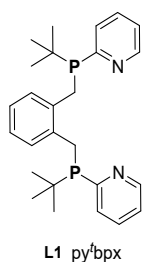
L1 py^{t}bpx

The synthesis of diphosphine ligand L1 py^{t}bpx is nearly diastereoselctive and gives a mixture of two diastereomers C_2 (major) and C_s (minor) with an averaged ratio of $\approx$ 97:3 at room temperature. Material was provided by the group of Prof. Beller. Details on the preparative procedure can be found in the literature.[3]

The following NMR-data corresponds to the C_2 (major) diastereomer.

¹H NMR (300 MHz, CCl$_2$D$_2$) δ 8.76 (m, 2H), 7.58 − 7.44 (m, 4H), 7.23 − 7.18 (m, 2H), 6.98 − 6.94 (m, 2H), 6.75 − 6.70 (m, 2H), 3.94 (dd, J(H,H) = 13.4, J(H,P) = 4.6 Hz, 2H), 3.26-3.16 (m, J(H,H) = 13.4 Hz, 2H), 1.10 (d, ^{2}J(H,P) = 11.8 Hz, 18H).
³¹P{¹H} NMR (122 MHz, CCl$_2$D$_2$) δ 8.91 (s). (major diastereomer, 97 % based on integration)
¹⁵N NMR (40 MHz, CCl$_2$D$_2$) δ -51.3 (s).
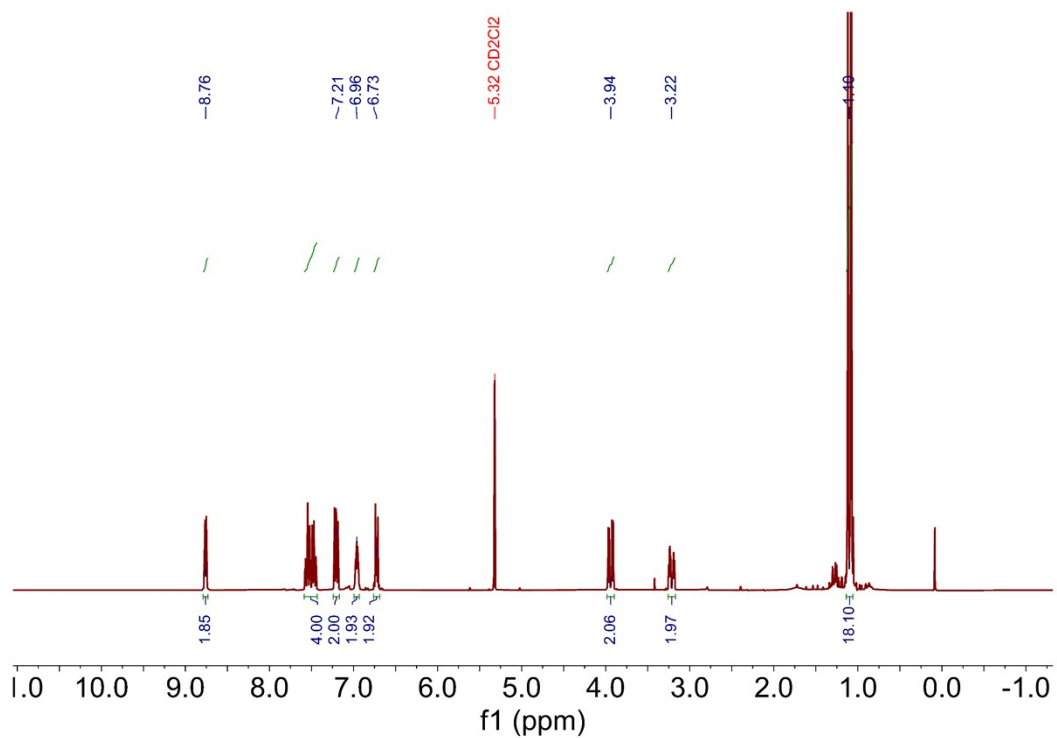
Figure SI-1 ^{1}H-NMR spectrum of **L1** in CCl$_2$D$_2$ at rt and ap.
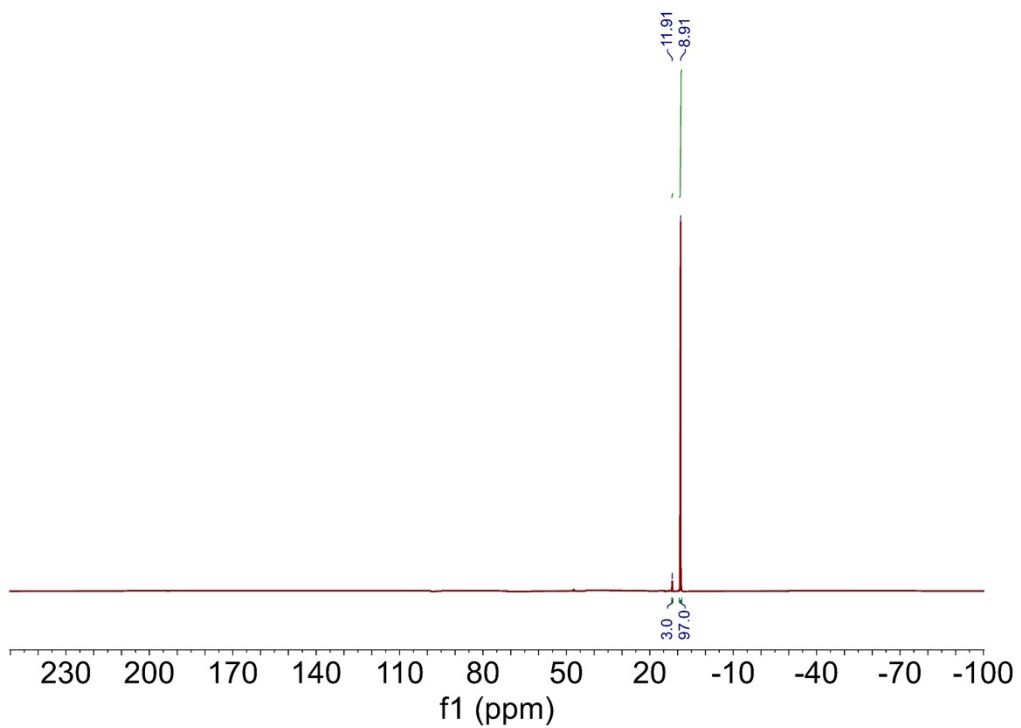
Figure SI-2 ^{31}P{^{1}H}-NMR spectrum of **L1** in CCl$_2$D$_2$ at rt and ap.
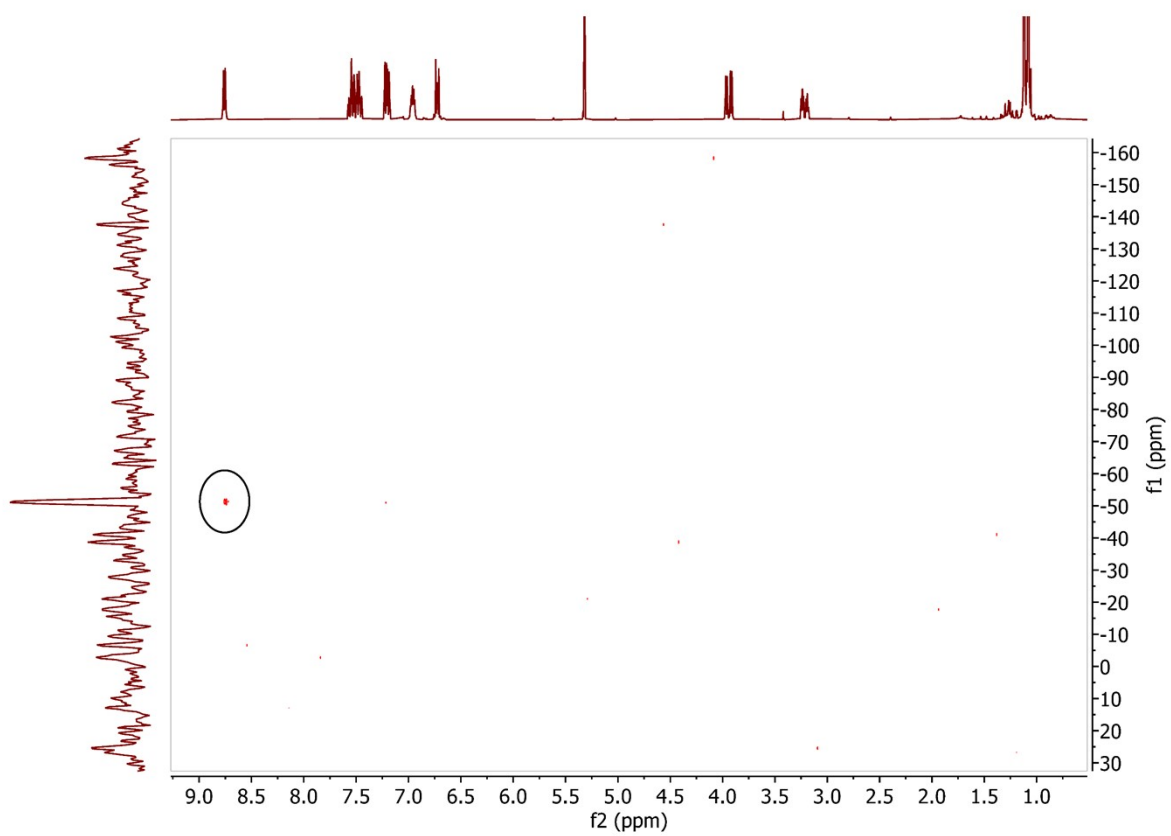
Figure SI-3 ^{1}H/^{15}N-HMBC-NMR spectrum of **L1** in CD_2Cl_2 at rt. Transfer delay 143 ms (J = 3.5 Hz).

Figure SI-X shows ^{31}P{^{1}H}NMR spectra of the mixture of C_2 and C_s diastereomers of **L1** in toluene-d8 at room temperature and after treatment at 120 °C for 12 h. Starting from a mixture of 3:97 (C_s:C_2) at room temperature, the thermal treatment leads to a 56:44 mixture (see also section SI-D:).

L1 (diastereomeric mixture)
Toluene-d8

Treatment at 120 °C (12h)
Measured at rt
56:44

8.15
(C_2)

11.11
(C_s)
Measured at rt
3:97

25 23 21 19 17 15 13 11 9 7 5 3 1 -1
f1 (ppm)

Figure SI-4 ^{31}P{^{1}H}-NMR of **L1** (mixture of C_2 and C_s) at room temperature and after thermal treatment at 120 °C in toluene-d8

Phosphine **L2**
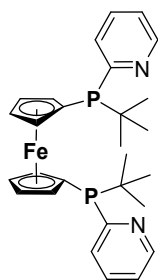
L2 py^{t}bpf

The synthesis of diphosphine ligand L2 py^{t}bpf gives a mixture of two diastereomers C_2 (major) and C_s (minor) with an averaged ratio of $\approx$ 70:30 at room temperature. Material was provided by the group of Prof. Beller. Details on the preparative procedure can be fined in the literature.[4]

The following NMR-data corresponds to the C_2 (major) diastereomer, which was enriched.

¹H NMR (300 MHz, dichloromethane-d_2) δ 8.76 (m, 2H), 7.81 (m, 2H), 7.68 (tt, J = 7.6, 2.0 Hz, 2H), 7.28 (m, 2H), 4.54 – 4.47 (m, 2H), 4.17 (m, 2H), 3.87 – 3.80 (m, 4H), 0.93 (d, $^3J_{H,P}$ = 12.4 Hz, 18H).
³¹P{¹H} NMR (122 MHz, dichloromethane-d_2) δ 6.95 (s).
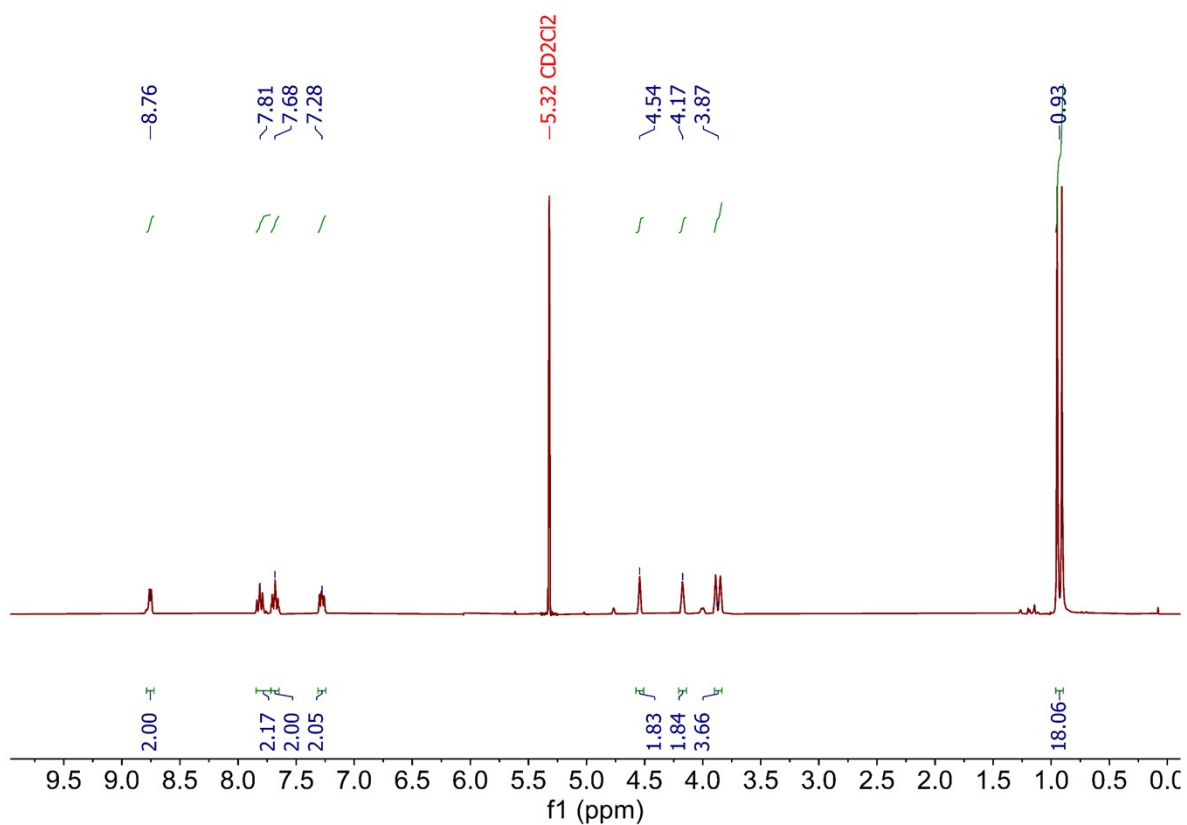
Figure SI-5 ^{1}H-NMR spectrum of **L2 (**C_2 diastereomer (major), enriched) in CD_2Cl_2 at rt and ap.
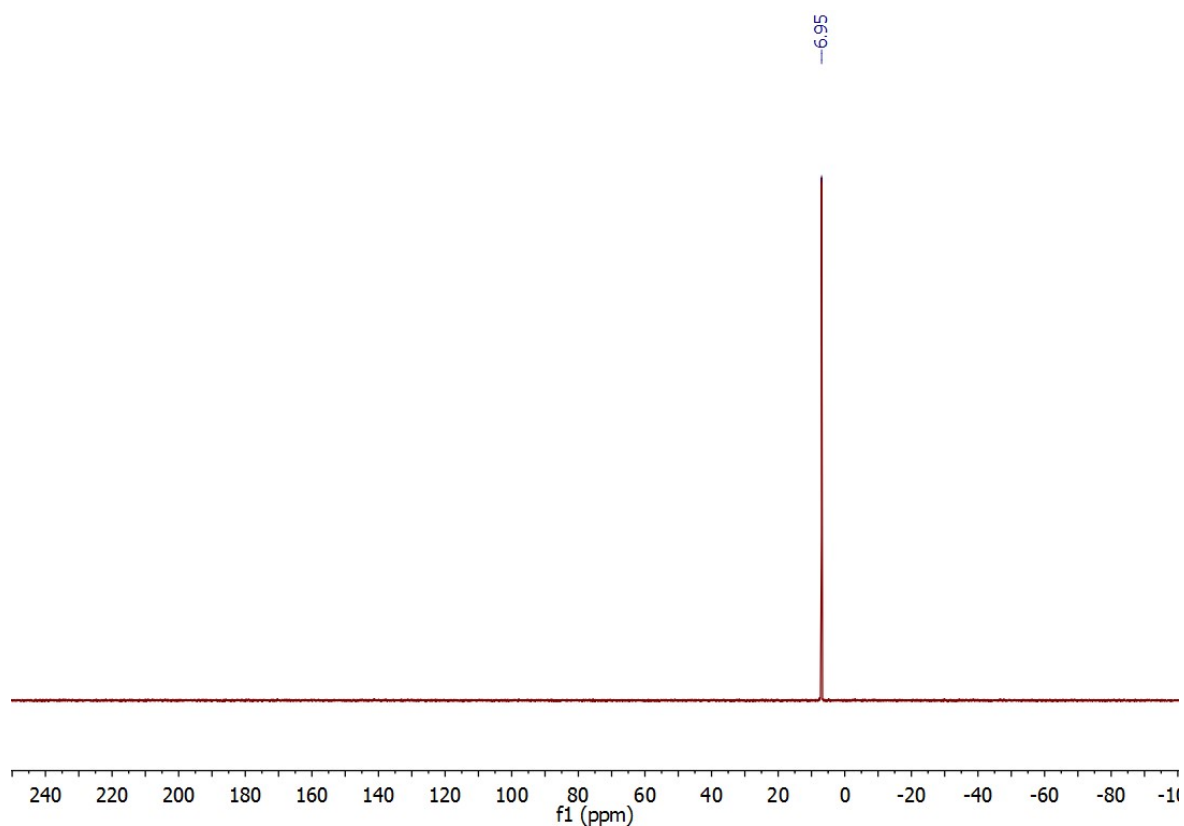
Figure SI-6 ^{31}P{^{1}H}-NMR of **L2** (C_2 diastereomer (major), enriched) in CD_2Cl_2 at rt and ap.
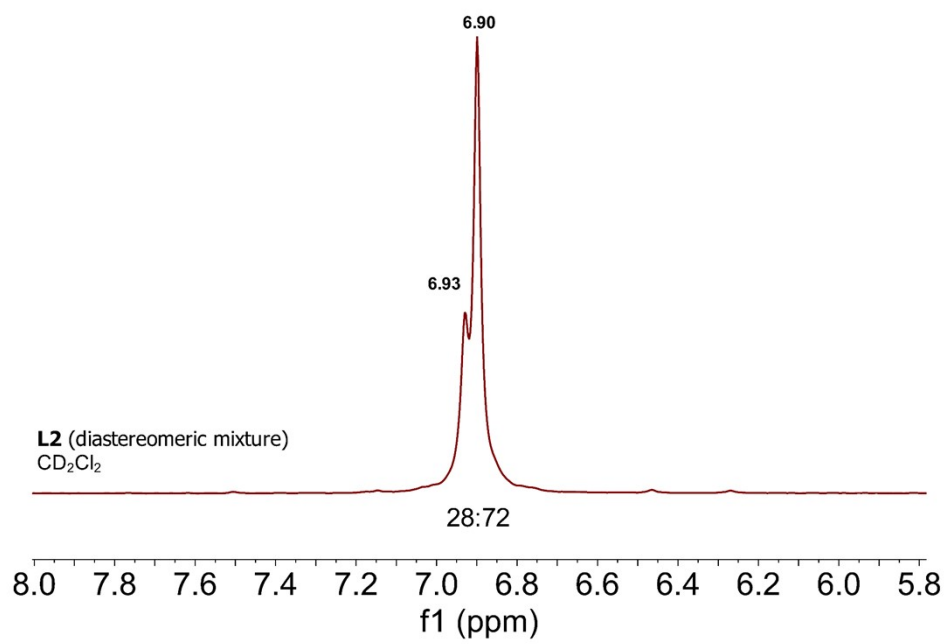
Figure SI-7 $^{31}P\{^1H\}$-NMR of **L2** (mixture of C_2 (major) and C_s (minor)) in CD_2Cl_2 at rt and ap.

^{15}N NMR (40 MHz, dichloromethane-d_2) δ -48.4 (s).
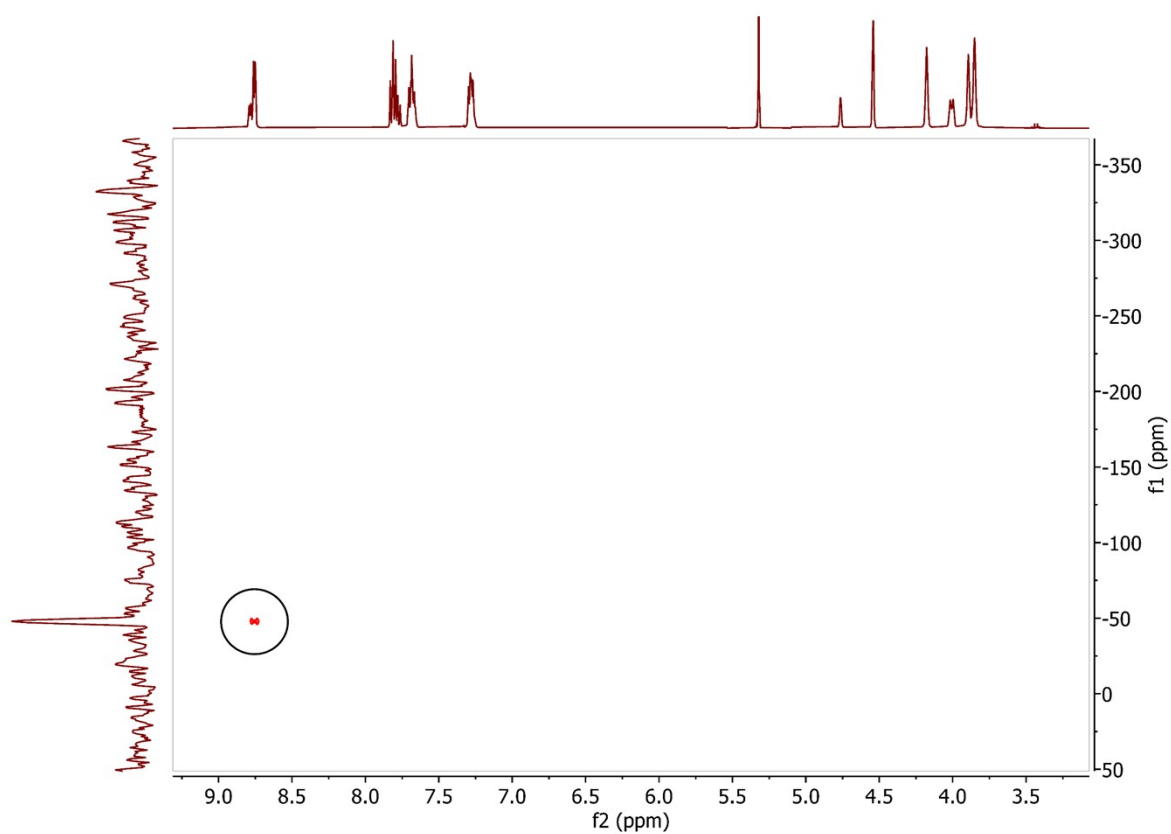
Figure SI-8 ^{1}H/^{15}N-HMBC-NMR spectrum of **L2** (mixture of C_2 and C_s) in CD_2Cl_2 at rt. Transfer delay 62.5 ms (J = 8 Hz). Only the dominating stereoisomer is showing up in the F_1 direction.

Figure SI-9 shows $^{31}P\{^1H\}$NMR spectra of mixture of C_2 and C_s diastereomers in toluene-d8 of **L2** at room temperature and after treatment at 120 °C for 12 h. Starting from a mixture of 28:72 ($C_s:C_2$) at room temperature, the thermal treatment leads to a 50:50 mixture.

L2 (diastereomeric mixture)
Toluene-d8

Treatment at 120 °C (12h)
Measured at rt

50:50

6.45
(C_2)

6.59
(C_s)

Measured at rt

28:72
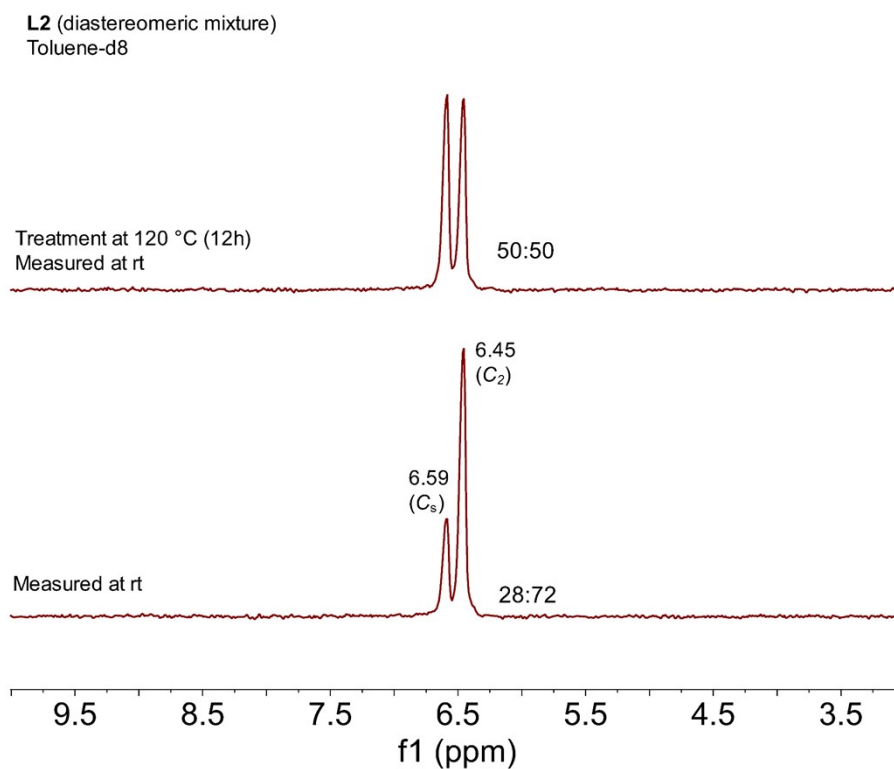
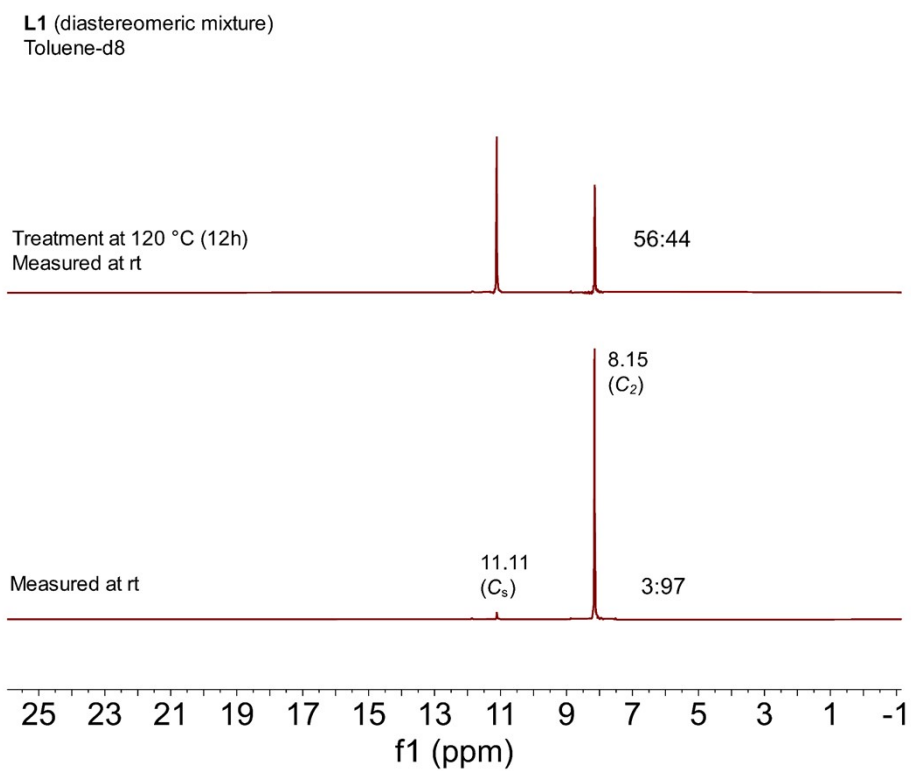**Figure SI-9** $^{31}P\{^1H\}$-NMR of **L2** (mixture of C_2 and C_s) at room temperature and after thermal treatment at 120 °C in toluene-d8

Phosphine **L3**

^{1}H NMR (300 MHz, dichloromethane-d_2) δ 7.50 – 7.39 (m, 2H, 4,5-Ar-*H*), 7.02 – 6.91 (m, 2H, 3,6-Ar-*H*), 3.00 – 2.92 (m, 4H, Ar-C*H$_2$*-P), 1.05 (d, $^3J_{H,P}$ = 10.7 Hz, 36H, *t*Bu-*H*).

^{13}C NMR (75 MHz, dichloromethane-d_2) δ 139.16 (dd, $^2J_{C,P}$ = 9.7 Hz, $^3J_{C,P}$ = 2.8 Hz, 1,2-Ar-*C*), 130.87 (d, $^3J_{C,P}$ = 15.3 Hz, 3,6-Ar-*C*), 124.98 (d, $^4J_{C,P}$ = 1.9 Hz, 4,5-Ar-*C*), 31.77 (d, $^2J_{C,P}$ = 23.3 Hz, P-*C*-(CH$_3$)$_3$), 29.67 (d, $^3J_{C,P}$ = 13.3 Hz, P-C-(*C*H$_3$)$_3$), 26.57 (dd, $^2J_{C,P}$ = 24.7 Hz, $^4J_{C,P}$ = 5.3 Hz).

^{31}P{^{1}H} NMR (122 MHz, dichloromethane-d_2) δ 26.06 (s).
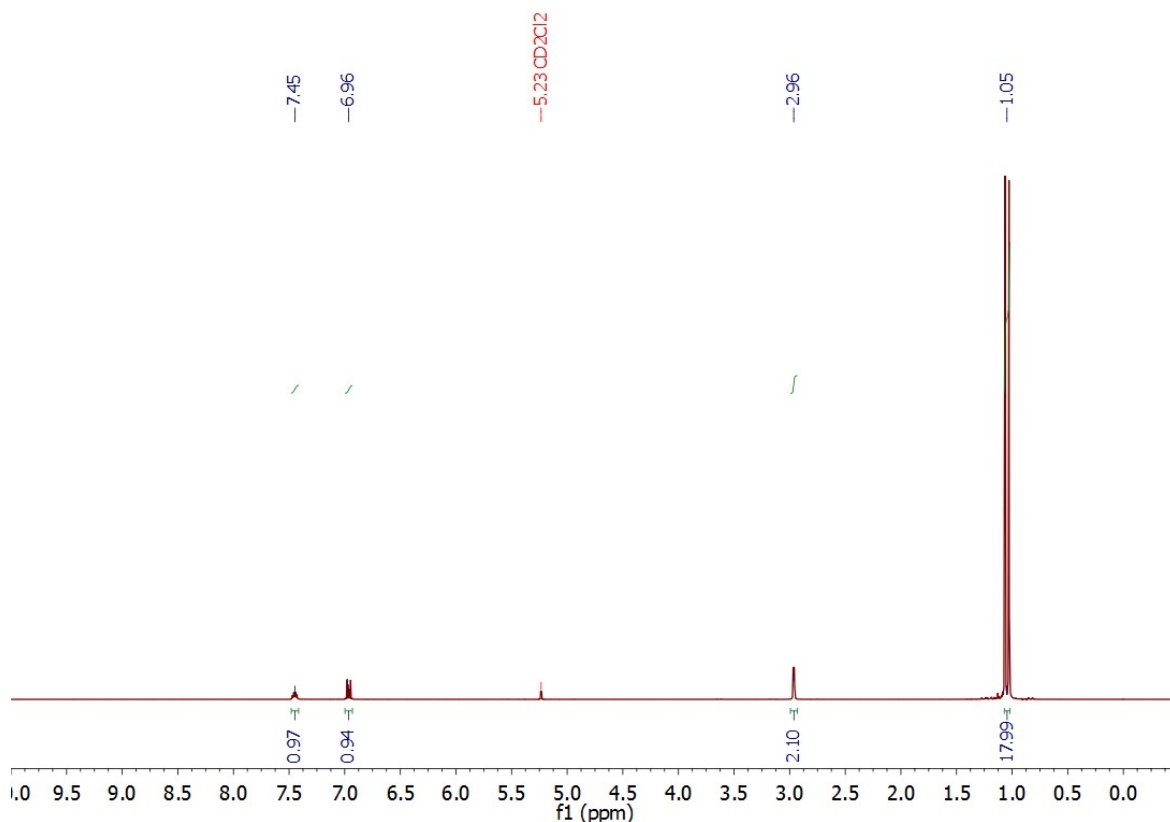
Figure SI-10 ^{1}H-NMR spectrum of **L3** in CD$_2$Cl$_2$ at rt and ap.

139.16
130.86
124.98
53.39
31.78
29.67
26.59

270 260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
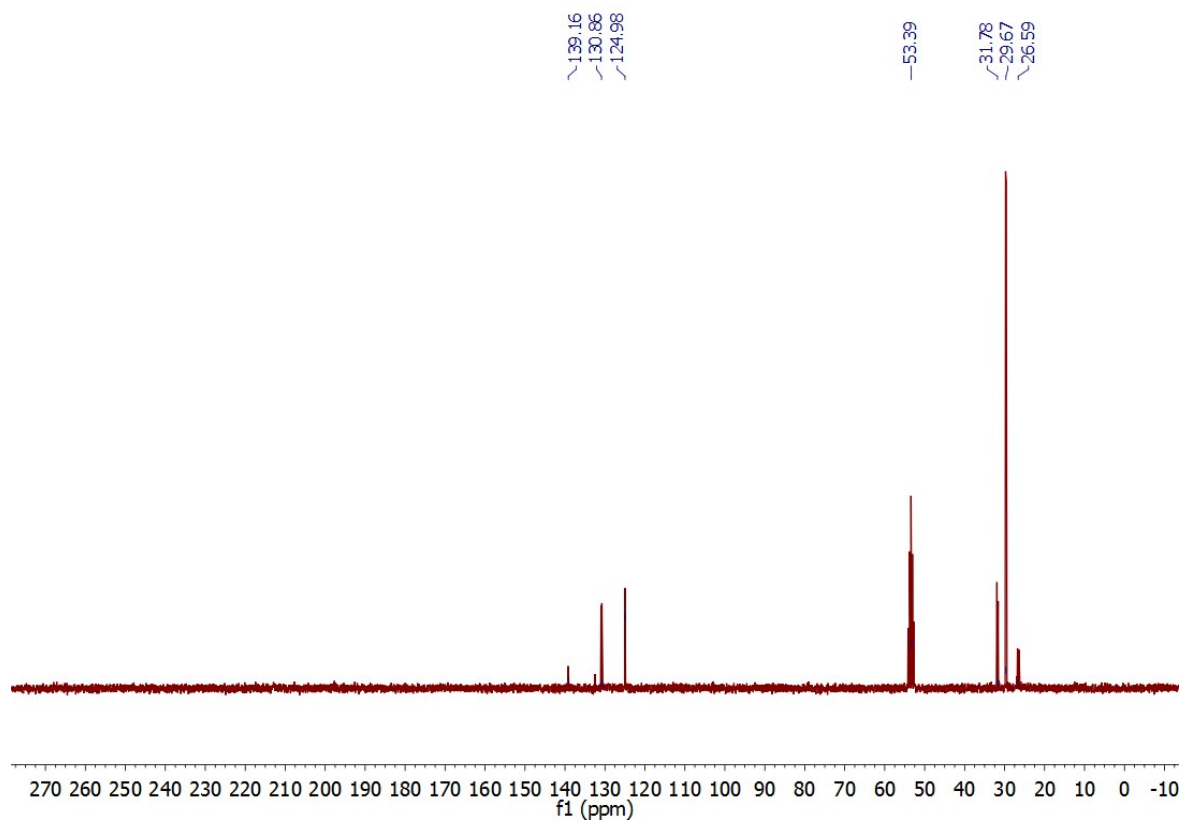
Figure SI-11 ^{13}C-NMR spectrum of **L3** in CD_2Cl_2 at rt and ap.

26.06

240   220   200   180   160   140   120   100   80   60   40   20   0   -20   -40   -60   -80   -10
f1 (ppm)
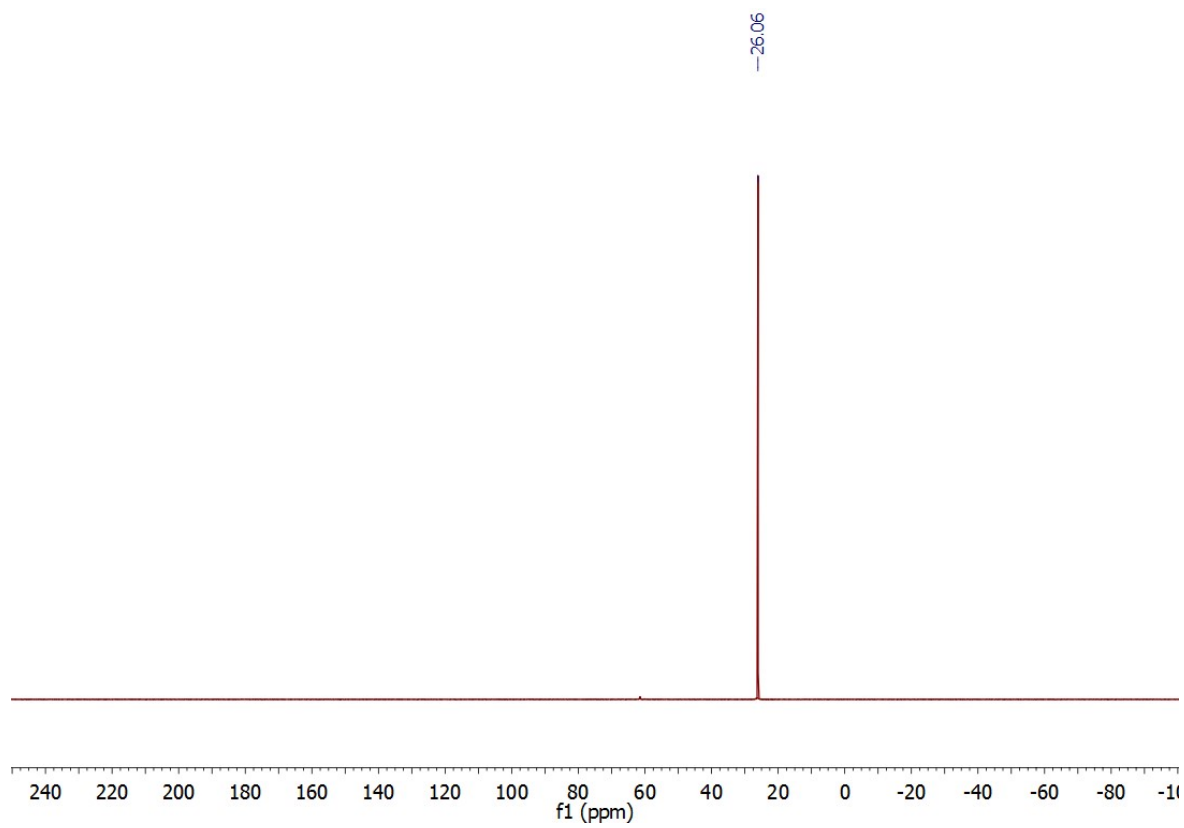
Figure SI-12 ^{31}P{^{1}H}-NMR spectrum of **L3** in CD_2Cl_2 at rt and ap.

SI-14

SI-C: Separation and assignment of pure diphosphine diastereomers

Determining the absolute configuration of L1

From the epimerized ligand **L1** the borane adducts were synthesized and the diastereomers were separated by column chromatography. An X-ray crystallographic analysis from the second fraction shows clearly the configuration of *meso*-**L1**-BH$_3$ in the crystal. By comparison of the NMR data of the free ligand and the regular synthesized ligand **L1** shows, that the major component of **L1** is the *rac*-diastereomer.

Synthesis of *meso*-L1-BH$_3$
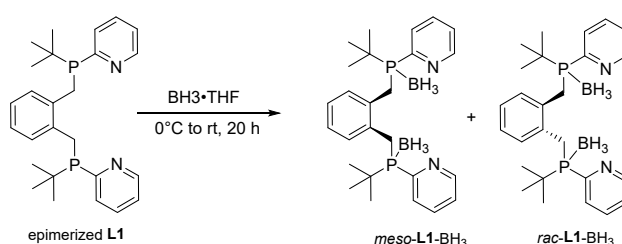
2.2 g of ligand **L1** was given in a 100 mL round flask with argon connection and dissolved in 20 mL toluene. The clear solution was heated to 100 °C for 2 h to epimerizing the ligand **L1**. The solvent was removed in high vacuum and the sticky oil was solved in 10 mL THF. The clear solution was cooled with ice and 9.14 mL (9.14 mmol) of a 1M BH$_3$·THF solution was dropped. After 30 min the ice bath was removed, and the reaction mixture was stirred for 4 h. An TLC shows the two diastereomers at Rf = 0.14 and Rf = 0.23 (1:5 EE/Hept). The borane adducts were separated by chromatography using the Combi Flash apparatus running 5 minutes with pure heptane, then increasing the ethyl acetate to 10 % in 35 min. The fraction with the mixture of diastereomers was disposed. 384 mg product *rac*-**L1**-BH$_3$ of the first fraction was collected and 541 mg (53%) product of the second fraction give the pure *meso*-**L1**-BH$_3$ borane protected ligand. A crystal suitable for X-ray structure was obtained from the chromatographed sample by evaporating the eluent.

^{1}H NMR (300 MHz, CDCl$_3$) δ 8.81(d, J = 4.2 Hz, 2H, py), 7.87 (pseudo t, J = 6.4 Hz, 2H, py), 7.67 (m, 2H, py), 7.34 (m, 2H, py), 6.90 (m, 2H, benzene), 6.83 (m, 2H, benzene), 4.06 (d, J = 17.2 Hz, 1H, CH2), 4.01 (d, J = 17.2 Hz, 1H, CH2), 3.56 (d, J = 5.7 Hz, 1H, CH2), 3.51 (d, J = 5.7 Hz, 1H, CH2), 1.29 (d, J = 13.4 Hz, 18H, tBu), 1.13-0.05 (BH3), ^{13}C NMR (75 MHz, CDCl3) δ 152.6, 151.8, 148.9, 148.8, 136.3, 136.1, 132.4, 132.3, 132.1, 138.8, 131.2, 126.1, 125.1 (CH arom), 30.6, 30.2 (CH2), 25.9 (CH3,tBu), 23.2, 22.8 (C, tBu). ^{31}P NMR (121 MHz, C6D6): δ 38.52 (J = 50.3 Hz). (EI) *m:z* (relative intensity) [M-tBu]$^+$, 379 (100), 324 (13), 323 (64). EA

calcd for $C_{26}H_{40}B_2N_2P_2$: C, 67.28; H, 8.69; N, 6.04, P,13.35. Found: C, 67.35; H, 8.67; N, 6.07, P,13.00.

Synthesis of the free ligand *meso*-L1

541 mg (1.16 mmol) of *meso*-**L1**-BH$_3$ was suspended in 15 mL absolute morpholine. The clear solution was warmed up at 50 °C for 3 h. According to TLC the reaction is complete and only free ligand was detected (Rf = 0.57, 2:1 (Hept/EE)). In high vacuum the morpholine was removed and the sticky colorless residue was chromatographied under argon with the eluent 2:1 (Hept/EE). After evaporating the solvent in high vacuum 407 mg (80%) of free *meso*-**L1** was achieved.

^{1}H NMR (300 MHz, C$_6$D$_6$) δ 8.58(dm, J = 4.7 Hz, 2H, py), 7.38 (m, 2H, py), 7.29 (tm, J = 6.8 Hz, 2H, py), 6.38 (m, 4H, CH arom), 6.54 (m, 2H, CH arom), 4.37 (dd, J = 14.0 Hz, J =) 5.0 Hz, 2H, CH2), 3.59 (dd, J = 13.8 Hz, J = 2.2 Hz, 2H, CH2), 1.20 (d, J = 10.9 Hz, 18H, tBu). ^{31}P NMR (121 MHz, C6D6): δ 13.35. HRMS (ESI) m/z$^+$calcd for $C_{26}H_{34}N_2P_2$ (M+1)$^+$ 437.2275; found 437.2267.

Determining the absolute configuration of L2

The diastereomeric mixture of **L2** was protected by BH$_3$·THF, separated by column chromatography and deprotected with morpholine. Next, from the diastereomeric pure *rac*-**L2** and *meso*-**L2** the corresponding palladium complexes of the type [**L2**Pd(C$_5$H$_5$NO$_2$)] (C$_5$H$_5$NO$_2$: N-methylmaleimide) were prepared. The absolute configuration was found by comparison the NMR data of complexes [(**L2**-*rac*)Pd(C$_5$H$_5$NO$_2$)] and [(**L2**-*meso*)Pd(C$_5$H$_5$NO$_2$)] with the NMR spectra of the crystals [(**L2**-*rac*)Pd(C$_5$H$_5$NO$_2$)] used for the X-ray structure analysis (see below).

Synthesis of the borane protected diastereomeric ligands L2-*rac* and L2-*meso*
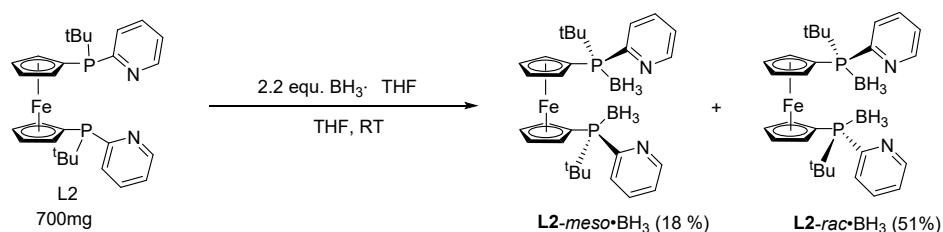
In a 50 mL round flask with argon connection and stirring bar 700 mg (1.36 mmol) ligand **L2** (70:30 diastereomere mixture) was dissolved in 10 mL THF. To the clear orange solution 3 mL (3.0 mmol) of a 1M borane solution was added. After stirring overnight, the borane adducts was chromatographied by the Combi Flash apparatus running 5 minutes with pure heptane and the polarity was increased

in 35 minutes to 5% ethyl acetate. 132 mg (18%) of the ligand **L2**-*meso* symmetry and 376 mg (51%) of ligand **L2**-*rac* symmetry were obtained as an orange solid.

Diastereomer L2-*rac*·BH₃: ^{1}H NMR (300 MHz, CDCl₃): δ 8.88 (m, 2H, py), 8.28 (m, 2H, py), 7.85 (m, 2H, py), 7.47 (m, 2H, py), 4.73 (m, 2H, ferrocenyl), 4.67 (m, 2H, ferrocenyl), 4.29 (m, 2H, ferrocenyl), 3.57 (m, 2H, ferrocenyl), 0.98 (d, J = 14.6 Hz, 18H, tBu), 1.61-0.25 (br, BH₃). ^{13}C NMR (75 MHz, CDCl₃): δ 154.8, 153.9, 149.3, 149.2, 135.7, 135.6, 130.5, 130.2, 124.8 (py), 76.3, 74.8, 74.7, 74.6, 73.2, 73.1, 66.1 and 65.3 (ferrocenyl), 31.4, 31.0 and 25.8 (tBu). ^{31}P NMR (121 MHz, C₆D₆) δ 30.1 (q(br), J = 63.7 Hz, P-BH₃); R_f = 0.15 Hep/EE 1:7). Yield 376 mg (51%) of orange solid.

Diastereomer L2-*meso*·BH₃: ^{1}H NMR (300 MHz, CDCl₃): δ 8.91 (m, 2H, py), 8.26 (m, 2H, py), 7.83 (m, 2H, py), 7.44 (m, 2H, py), 5.25 (m, 2H, ferrocenyl), 4.24 (m, 2H, ferrocenyl), 4.07 (m, 2H, ferrocenyl), 3.62 (m, 2H, ferrocenyl), 0.99 (d, J = 14.0 Hz, 18H, tBu), 1.54-0.19 (br, BH₃); ^{13}C NMR (75 MHz, CDCl₃): δ 154.7, 153.7, 149.7, 149.6, 135.6, 135.4, 130.3, 130.0, 124.8, 124.7 (Py), 76.1, 75.6, 75.9, 75.2, 74.7, 74.6, 72.9, 72.7, 66.3 and 65.5 (ferrocenyl), 31.4, 30.9, 25.8, and 25.7 (tBu), ^{31}P NMR (121 MHz, C₆D₆) δ 29.9 (q (br), J = 68.1 Hz, P-BH₃), R_f = 0.31 Hep/EE 1:7), yield 132 mg (18%) of orange solid.

Synthesis of the free ligands L2-*meso* and L2-*rac* by deprotecting with morpholine

L2-*rac*: In a 50 mL flask with argon connection and stirring 376 mg of **L2**-*rac*·BH₃ adduct was suspended in 7 mL absolute morpholine. The orange suspension was heated on the water bath at 50 °C. According to the TLC after 4 hours the reaction was complete. The morpholine was removed in high vacuum and the orange residue was chromatographed under argon with the eluent 2:1 (heptane/ethyl acetate). The eluent was saturated by argon for one hour before using it as eluent. After removing the solvent in high vacuum 312mg (87%) of a sticky yellow oil was obtained.

^{1}H NMR (300 MHz, C₆D₆): δ 8.58 (m, 2H, py), 7.72 (t,t, J = 7.8 Hz, 1.3 Hz, 2H, py), 7.02 (t,t, J = 7.6 Hz, J = 2.1 Hz, 2H, py), 6.68-6.62 (m, 2H, py), 4.93 (m, 2H, ferrocenyl), 4.37 (m, 2H, ferrocenyl), 3.95 (m, 4H, ferrocenyl), 1.13 (d, J = 12.0 Hz, 18H, tBu). ^{13}C NMR (75 MHz, CDCl₃): δ 163.6 and 163.4 (C), 149.6, 149.5, 134.6, 134.4, 132.6, 131.9, 122.7 (py), 78.5, 77.9, 74.0, 73.9, 73.7, 72.5, 71.7, 71.5 (ferrocenyl), 31.8 31.6, 28.3 and 28.1 (tBu), ^{31}P NMR (121 MHz, C₆D₆) δ 7.03. HRMS (ESI) m/z⁺calcd for C₂₈H₃₄FeN₂P₂ (M+H)⁺ 517.16197; found 517.16221.

L2-*meso*: Analogous 318mg of **L2**-*meso*·BH$_3$ adduct was deprotected by morpholine and 219 mg (73%) of free orange ligand was achieved.

^{1}H NMR (300 MHz, C$_6$D$_6$): δ 8.63 (m, 2H, py), 7.72 (t,t, J = 7.8 Hz, 1.1 Hz, 2H, py), 7.04 (t,t, J = 7.6 Hz, J = 2.1 Hz, 2H, py), 6.66 (m, 2H, py), 5.17 (m, 2H, ferrocenyl), 4.17 (m, 2H, ferrocenyl), 4.05 (m, 2H, ferrocenyl), 3.95 (m, 2H, ferrocenyl), 1.11 (d, J = 12.3 Hz, 18H, tBu). ^{13}C NMR (75 MHz, C$_6$D$_6$): δ 163.5 and 163.3 (C), 149.7, 149.6, 134.5, 134.3, 132.4, 131.8 and 122.6 (py), 77.9, 77.4, 74.1, 74.0, 73.8, 72.3, 71.5 and 71.4 (ferrocenyl), 31.7, 31.5, 28.2 and 28.0 (tBu), ^{31}P NMR (121 MHz, C$_6$D$_6$) δ 7.2. HRMS (ESI) m/z$^+$calcd for C$_{28}$H$_{34}$FeN$_2$P$_2$ (M+H)$^+$ 517.16197; found 517.162109.

Synthesis of the palladium complexes [(L2-*rac*)Pd(C$_5$H$_5$NO$_2$)] and [(L2-*meso*)Pd(C$_5$H$_5$NO$_2$)]

L2-*rac* or **L2**-*meso*   [(**L2**)Pd(C$_5$H$_5$NO$_2$)]
L2: **L2**-*rac* or **L2**-*meso*
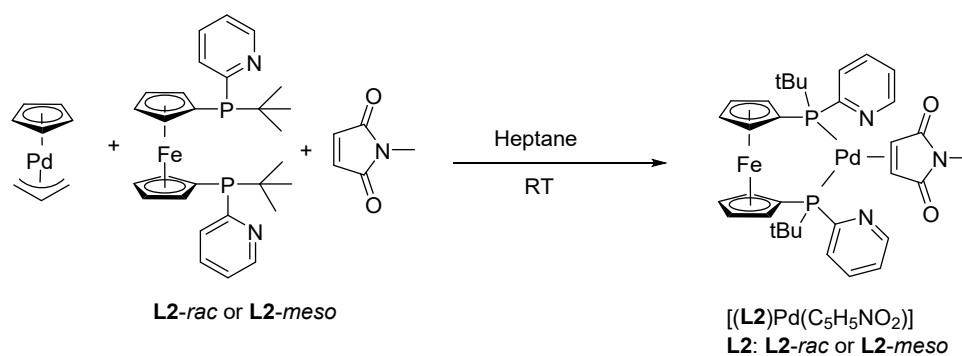
[(L2-*rac*)Pd(C$_5$H$_5$NO$_2$)]: In a Schlenktube with stirring bar 58.1 mg (0.274 mmol) of (η^3-allyl)(η^5-cyclopentadienyl)palladium precursor [literatur: Sanshiro Komiya, Synthesis of Organometallic compounds, A Practical Guide, 1997 John Wiley & Sons, p. 290] was solved in the glove box in 5 mL absolute heptane. In a second Schlenk flask 150 mg (0.274 mmol) **L2**-*rac* and 30.4 mg (0.274mmol) N-methylmaleinimide were solved in 6 mL of 60°C warm heptane to get a clear orange solution. Cooled at room temperature this solution was added slowly to the dark red solution with the palladium precursor. The reaction mixture become brighten and a yellow precipitate was obtained. At the next day the solution was filtered, and the yellow precipitate was washed 2 times with heptane. After drying in high vacuum 200 mg (95%) of the complex [(**L2**-*rac*)Pd(C$_5$H$_5$NO$_2$)] was obtained with high purity.

^{1}H NMR (300 MHz, C$_6$D$_6$): δ 8.48 (m, 2H, py), 8.12 (m, 2H, py), 7.13 (m, 1 H, py), 7.02 (t,t, J = 7.6 Hz, J = 2.3 Hz, 1H, py), 6.63 (m, 2H, py), 5.32 (m, 1H, CH), 4.89 (m, 1H, CH), 4.45 (m, 2H, CH), 3.95 (m, 1H, CH), 3.92 (m, 2H CH), 3.85 (m; 2H, CH), 3.44 (m; 1H, CH), 3.03 (s, 3H, NMe), 1.36 (d, J = 14.9Hz, 9H, tBu), 1.32 (d, J = 14.6Hz, 9H, tBu). ^{13}C NMR (75 MHz, C$_6$D$_6$): δ 175.9 and 175.8, 160.2, 159.7, 158.5 and 158 (C), 149.5, 149.4, 135.6, 135.4, 135.1, 135.0, 134.8, 134.5, 133.9, 124.3,

123.9 (py), 78.6, 78.3, 76.8, 76.5, 75.0, 74.8, 74.4, 74.2, 73.8, 73.4, 72.7, 72.6, 72.5, 71.0, 70.5, 70.4 (ferrocenyl), 52.6, 52.5, 52.2, 52.1, 51.1, 51.0, 50.7, 50.6 (maleinimide), 35.5 35.3, 35.1, 28.1, 28.0, 27.4, 27.3 (tBu), 23.5 (NMe), ^{31}P NMR (121 MHz, C_6D_6) δ 47.3 (d, J = 16Hz), 46.4 (d, J = 16Hz). EA calcd for $C_{33}H_{39}FeN_3O_2P_2Pd$: C, 54.01; H, 5.36; N, 5.73; P,8.44. Found: C, 53.44; H, 5.48; N, 5.72; P,8.48.

[(L2-*meso*)Pd(C$_5$H$_5$NO$_2$)]: In analogous manner the complex [(L2-*meso*)Pd(C$_5$H$_5$NO$_2$)] was prepared starting from 91 mg (0.176 mmol) **L2**-*meso*, 19 mg (0.167 mmol) N-methyl maleinimide, 35.4 mg (0.167mmol) (η^3-allyl)(η^5-cyclopentadienyl)palladium giving 98 mg (80%) of yellow product.

^{1}H NMR (300 MHz, C_6D_6): δ 8.27 (m, 2.77H, py), 7.74 (t, J = 7.3 Hz, 2H, py), 7.62 (m, 0.77 H, py), 6.81 (t,t, J = 7.7 Hz, J = 2.2 Hz, 2H, py), 6.66 (t,t, J = 7.7 Hz, J = 2.1 Hz, 0.77H, py), 6.39 (m, 2.77H, py), 4.66 (m, 0.77H, CH), 4.49 (m, 2H, CH), 4.42 (m, 0.77H, CH), 4.33 (m, 2H, CH), 4.27 (m; 2H, CH), 4.19 (m; 0.77H, CH), 4.05 (m; 2.77H, CH), 3.95 (m; 2.77H, CH), 3.10 (s, 3H, NMe), 3.03 (s, 1.21H, NMe), 1.36 (d, J = 13.9Hz, 25.26H, tBu). ^{31}P NMR (121 MHz, C_6D_6) δ 46.9 and 46.3. HRMS (ESI) m/z$^+$calcd for $C_{33}H_{39}FeN_3O_2P_2Pd$ (M+1)$^+$ 734,0980; found 734,0991.

The complex [(**L2**-*rac*)Pd(C$_5$H$_5$NO$_2$)] is asymmetric and has C_1 symmetry. Therefore, the two phosphorous atoms are coupling each other and are showing in ^{31}P NMR two doublets. By contrast the complex [(**L2**-*rac*)Pd(C$_5$H$_5$NO$_2$)] has C_s symmetry and because of the two orientations of N-methyl maleinimide the complex contains two distereomeres also both with C_s symmetry (ratio 77:28). In ^{31}P NMR two singlets are observed.

Preparation of crystals for X-ray analysis of [(L2-*rac*)Pd(C$_5$H$_5$NO$_2$)] and assignment of the configuration of the ligands L2-*rac* and L2-*meso*

42 mg of diastereomeric [(**L2**)Pd(C$_5$H$_5$NO$_2$)] complex mixture was dissolved in 2 mL toluene. Some toluene was removed in high vacuum, until the solution starts to get cloudy. The suspension was warmed up in a water bath and the clear solution was filtered under argon over Celite. The clear solution was put in the fridge and on the next day crystals are obtained. According to the crystal structure the complex contains the *rac*-**L2** ligand. Since the NMR data of the dissolved crystals [(**L2**-*rac*)Pd(C$_5$H$_5$NO$_2$)] used for X-ray analysis are identical with the NMR data of the synthesized complex made from pure **L2**-*rac* ligand the configuration of the dissolved ligands **L2**-*rac* and **L2**-*meso* can be distinguished.

¹H NMR (CDCl₃)
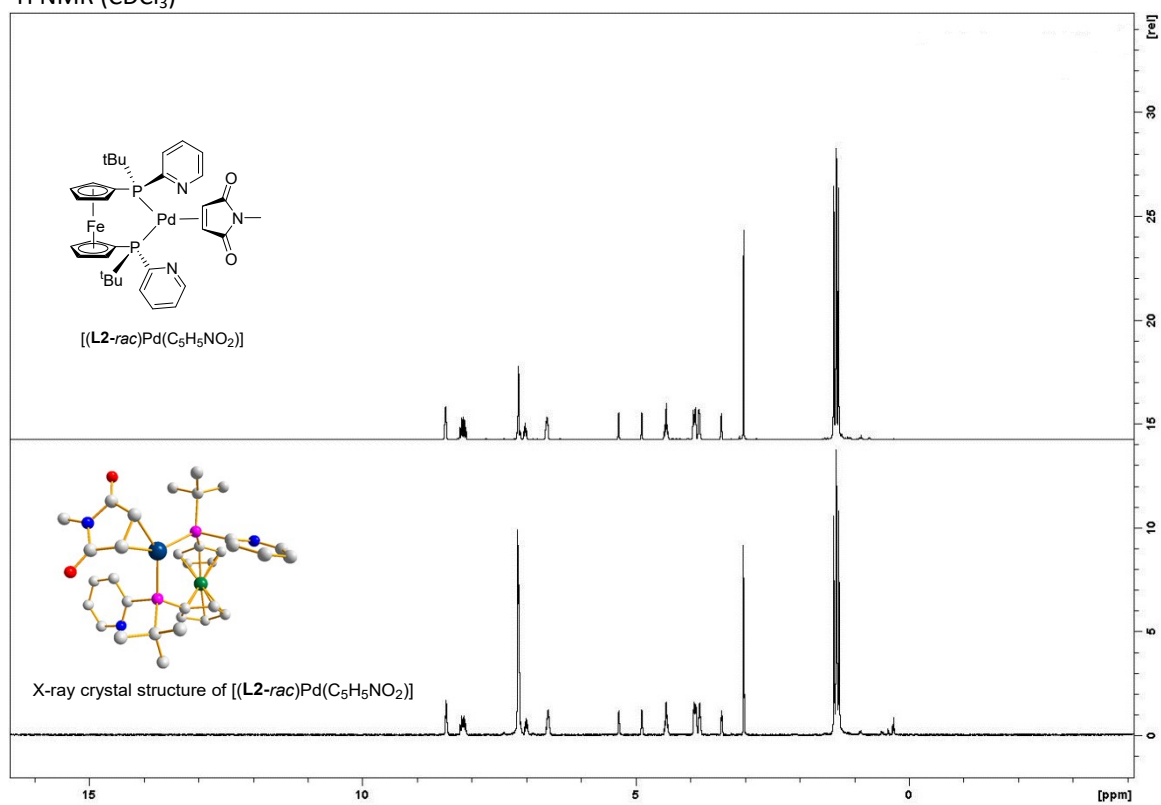
Figure SI-13   1H-NMR spectra of [(**L2**-*rac*)Pd(C₅H₅NO₂)] (above) directly from the complex synthesis and after dissolving single crystals used for X-ray crystal structure analysis.

SI-D: Kinetic experiments for the estimation of the inversion barrier of ligand epimerization

General experimental procedure

A 10 mL Schlenk flask was charged with diphosphine **L1** (0.06 mmol) and dissolved in 1 mL of dry toluene-d_8 under argon. The solution was stirred for a few minutes. The solution was then transferred into a J. Young NMR-tube for NMR spectroscopic experiments. The solution was heated to the desired temperature for certain time intervals and was measured after cooling to room temperature. These experiments have been conducted for θ = 80, 90 and 100 °C (T = 353, 363, 373 K).

Calculation[5,6]

The epimerization of C_2 symmetric (R,R and S,S) to the Cs symmetric (R,S and S,R; meso compound) diastereomer is reversible and results in a mixture of both compounds (Eq. 1). The conversion can be expressed by the rate equation (Eq. 2) by defining the forward and backward rate constants as k_{ep} and k_{rac}, respectively.

$$C_2 \quad \underset{k_{rac}}{\overset{k_{ep}}{\rightleftharpoons}} \quad C_s \qquad \qquad \textbf{Eq. 1}$$

$$\frac{dC_2}{dt} = -k_{ep}\,C_2 + k_{rac}\,C_s \qquad \qquad \textbf{Eq. 2}$$

The established equilibrium is expressed by Eq. 3 and the equilibrium constant K was calculated using Eq. 4. The molar ratio of diastereomers in equilibrium was determined by ^{31}P-NMR spectroscopy after heating a ligand solution (see general experimental procedures) in a J. Young NMR-tube for 12h and 24h at 120°C without noticing any further change in concentration.

$$t\to\infty \quad \frac{dC_2}{dt} = 0 = -k_{ep}\,C_2^{eq} + k_{rac}\,C_S^{eq} \qquad \qquad \textbf{Eq. 3}$$

$$\frac{k_{ep}}{k_{rac}} = \frac{C_S^{eq}}{C_2^{eq}} = K = \frac{56}{44} = 1.273 \qquad \textbf{Eq. 4}$$

The change of C_2 isomers at any point can be described by Eq. 5. Substitution using the boundary conditions (BC), result in Eq. 6 which finally can be integrated to obtain Eq. 7.

$$-\frac{dC_2}{dt} = \frac{dC_s}{dt} = \frac{dx}{dt} \qquad \textbf{Eq. 5}$$

$$\left.\begin{array}{l} t = 0 : C_2 = C_2^0 \\ t_x : C_2 = C_2^0 - x \\ t_x = \infty \quad C_2^{eq} = C_2^0 - x^{eq} \end{array}\right\} \qquad \textbf{BC}$$

$$\frac{dx}{dt} = \left(k_{ep} + k_{rac}\right)\left(x^{eq} - x\right) \qquad \textbf{Eq. 6}$$

$$\ln\left(\frac{x^{eq}}{x^{eq} - x}\right) = \left(k_{ep} + k_{rac}\right) t \qquad \textbf{Eq. 7}$$

After resubstituting of x values and insertion of the equilibrium constant K the epimerization constant k_{ep} can be derived from the slope of Eq. 8. To express the concentration of the C_2 symmetric diastereomer, ^{31}P-NMR-area percentage values were used.

$$\ln\left(\frac{C_2 - C_2^{eq}}{C_2^0 - C_2^{eq}}\right) = -k_{ep}\left(1 + \frac{1}{K}\right) t \qquad \textbf{Eq. 8}$$
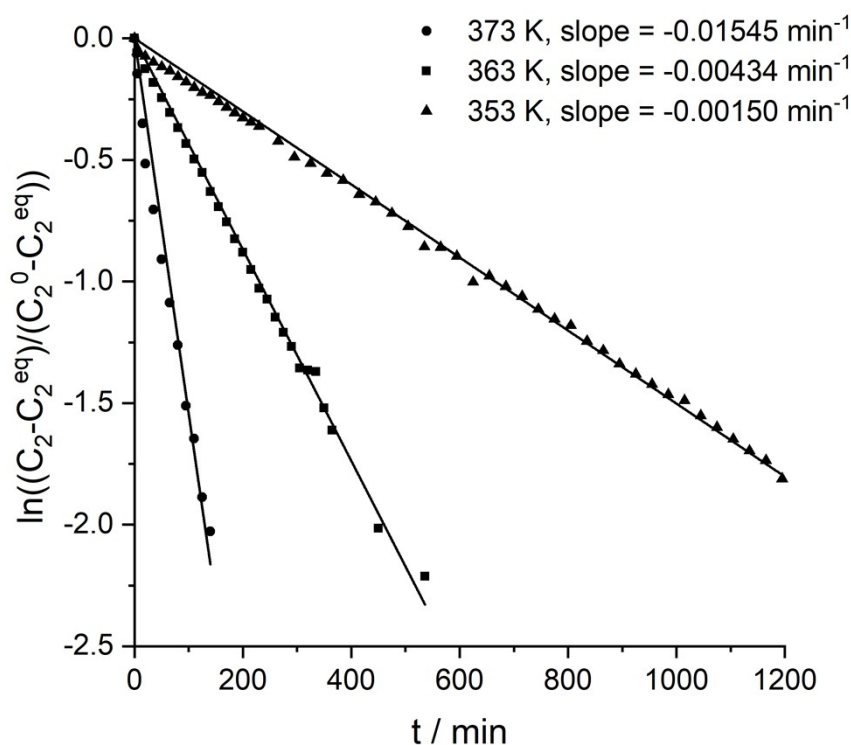
Figure SI-14 Plot of *ln((C₂-C₂ᵉᵠ)/(C₂⁰-C₂ᵉᵠ))* versus time for determination of epimerization rate constant k_{ep} for 373 K, 363 K and 353 K.

The Eyring equation (Eq. SI-9) and the Gibbs free energy equation (Eq. SI-10) was used to get equation (Eq. SI-11) from which the enthalpy and entropy of activation can be calculated. Here, k_B and h are the Boltzmann constant and the Plank constant, respectively. For that purpose an Eyring-plot is constructed ($ln(k/T)$ is plotted versus T^{-1}) from which the slope and the intercept allows for the calculation of $\Delta H^{\neq}$ and $\Delta S^{\neq}$.

$$k_{ep} = \frac{k_B T}{h} e^{\frac{-\Delta G_{inv}^{\ddagger}}{RT}} \qquad \textbf{Eq. 9}$$

$$\Delta G = \Delta H - T\Delta S \qquad \textbf{Eq. 10}$$

$$\ln\left(\frac{k_{ep}}{T}\right) = \frac{-\Delta H_{inv}^{\ddagger}}{R}\frac{1}{T} + \frac{\Delta S_{inv}^{\ddagger}}{R} + ln\left(\frac{k_{ep}}{h}\right) \qquad \textbf{Eq. 10}$$

intercept	21.21858 ± 2.83229
slope	-14966.61377 ± 1027.3403
R-sq	0.99531
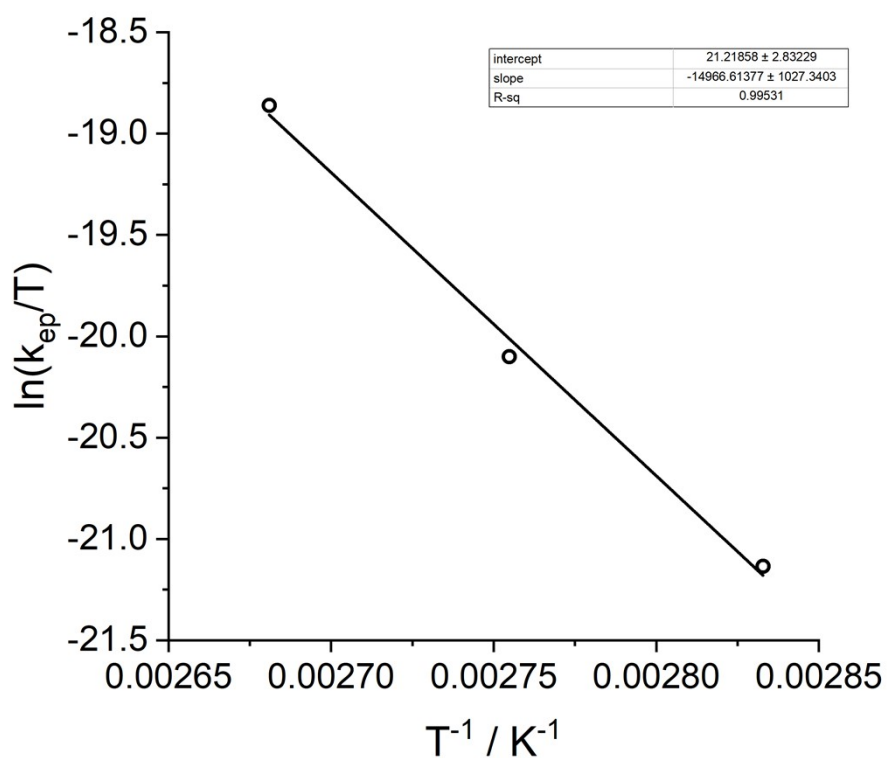
Figure SI-15   Eyring-Plot of $ln(k_{Ep}/T)$ versus T^{-1} for determination of activation parameters, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta G^{\ddagger}$.

The activation energy E_A result from the slope of the rearranged Arrhenius equation (Eq. 10) of previously determined epimerization rate constant (k_{ep}). Relevant kinetic data of the epimerization of py^{t}bpx (**L1**) are summarized in Table SI-1.

$$\ln(k_{ep}) = -\frac{E_A}{R}\frac{1}{T} + ln(A) \qquad\qquad \textbf{Eq. 10}$$

Intercept		36.30129 ± 2.84024
Slope		-15329.38422 ± 1030.2245
R-sq		0.9955
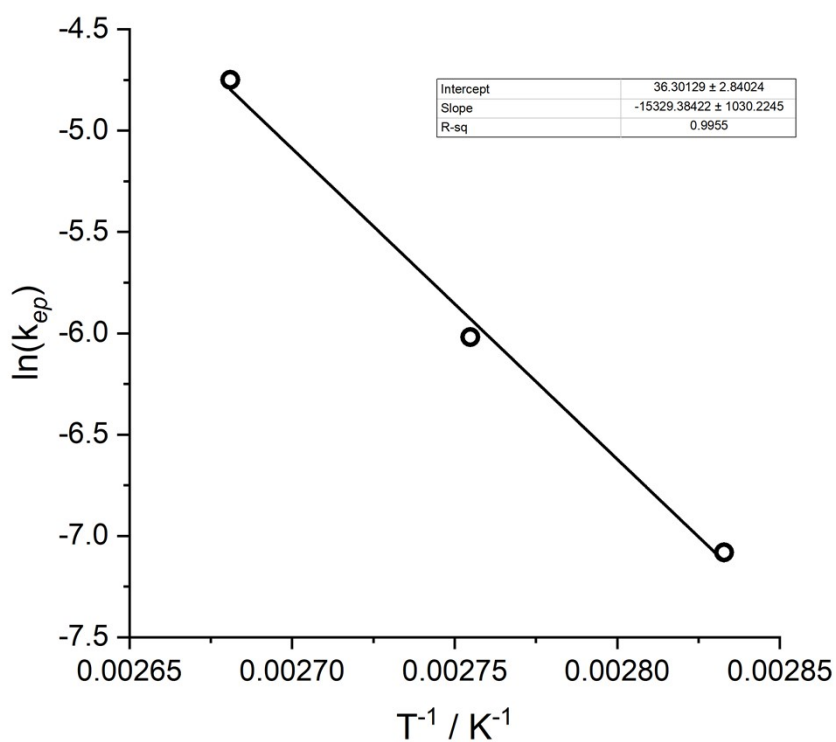
Figure SI-16   Arrhenius-Plot of $ln(k_{Ep})$ versus T^{-1} for determination of activation energy E_A.

Table SI-1   Epimerization rate constant (k_{ep}), activation parameters for inversion ($\Delta H^{\ddagger}_{inv}$, $\Delta S^{\ddagger}_{inv}$, $\Delta G^{\ddagger}_{inv}$) and activation energy (E_A) for py^{t}bpx (L1).

T	k_{ep} / min^{-1}	$\Delta H^{\ddagger}_{inv}$ / kJ mol^{-1}	$\Delta S^{\ddagger}_{inv}$ / kJ mol^{-1} K^{-1}	$\Delta G^{\ddagger}_{inv}$ / kJ mol^{-1}	E_A / kJ mol^{-1}
373	0.00865			106.8	
363	0.00243	124.4	-0.02113	107.7	127.4
353	0.00084			107.7	

SI-E: NMR-Characterization of diphosphine ligands (**L1**, **L2**, **L3**) in the presence of trifluoromethanesulfonic acid

CF$_3$SO$_3$H 2 equiv. (**L1**, **L2**)
CF$_3$SO$_3$H 5 equiv. (**L3**)
CD$_2$Cl$_2$

(?)

L1 = X$_1$, R = 2-pyridyl
L2 = X$_2$, R = 2-pyridyl
L3 = X$_1$, R = ^{t}Bu

X$_1$ X$_2$

L1 X$_1$, R = 2-pyridyl
L2 X$_2$, R = 2-pyridyl
L3 X$_1$,R = ^{t}Bu
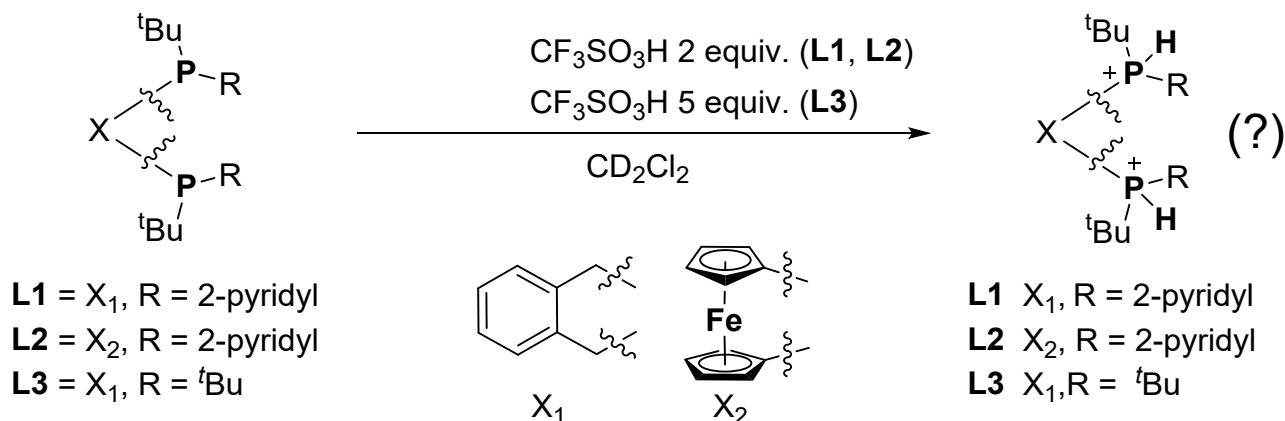
Stock solutions with dichloromethane-*d2* as solvent of diphosphine ligands (**L1, L2, L3** 0.03 mmol; 13.1 mg of **L1,** 15.5 mg **L2,** 11.8 mg of **L3**) have been prepared in a Schlenk flask. Prior to transfer, 2 equivalents (**L1**, **L2**) and 5 equivalents (**L3**) of trifluoromethanesulfonic acid (0.06 mmol, 0.15 mmol) were added with µL-Hamilton syringes and Schlenk flasks were thoroughly shaken after the addition. 0.6 mL of the solution were transferred into J. Young-NMR tubes.

<u>Phosphine **L1** / CF$_3$SO$_3$H</u>

^{1}H NMR (300 MHz, dichloromethane-d_2) δ 11.66 (s, 2H), 8.96 (ddd, $^3J_{H,H}$ = 5.6 Hz, $^4J_{H,H}$ = 1.7 Hz, $^5J_{H,H}$ = 0.7 Hz, 2H), 8.32 (dt, J = 7.8 Hz, J = 1.0 Hz, 2H), 8.14 (d, J = 7.8 Hz, 2H), 7.78 (tm, J = 6.7 Hz, 2H), 7.14 (m, 2H), 6.94 (dd, J = 5.7 Hz, J = 3.4 Hz, 2H), 3.84 (ddd, $^2J_{H,H}$ = 14.7 Hz, J = 3.1 Hz, J = 2.3 Hz, 2H), 3.45 (dd, $^2J_{H,H}$ = 14.9 Hz, J = 3.1 Hz, 2H), 1.16 (d, $^3J_{H,P}$ = 13.2 Hz, 18 H).
^{31}P NMR (122 MHz, dichloromethane-d_2) δ 8.09 (s).
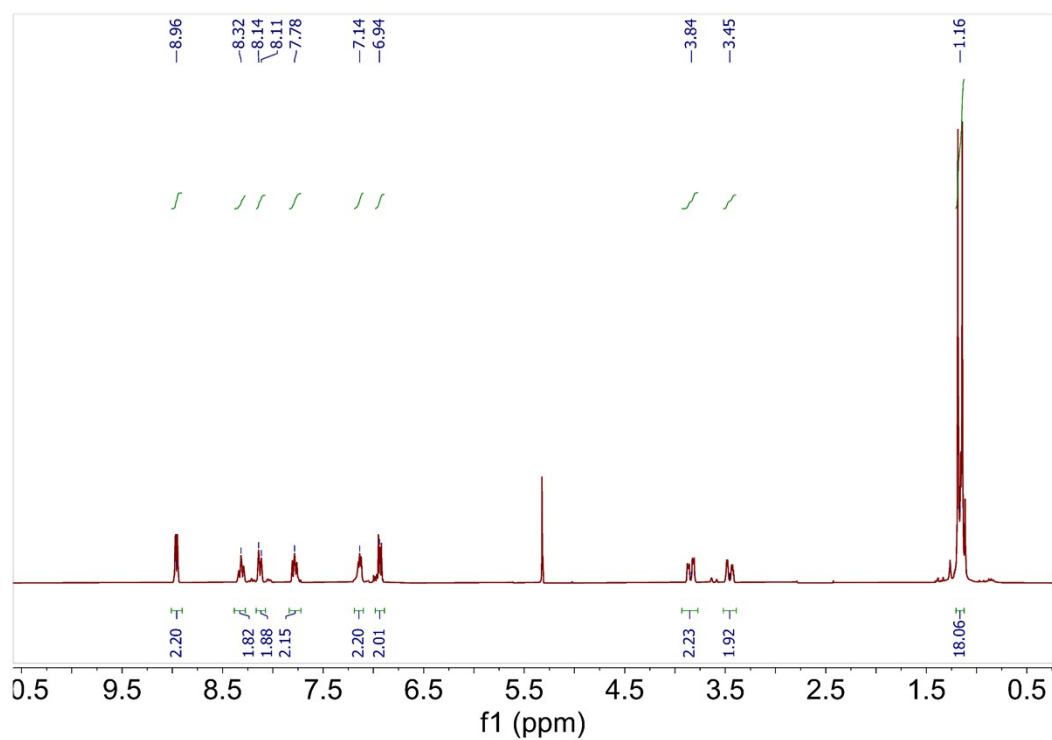
Figure SI-17   ¹H-NMR spectrum of the **L1** ligand in CD_2Cl_2/CF_3SO_3H at rt and ap.
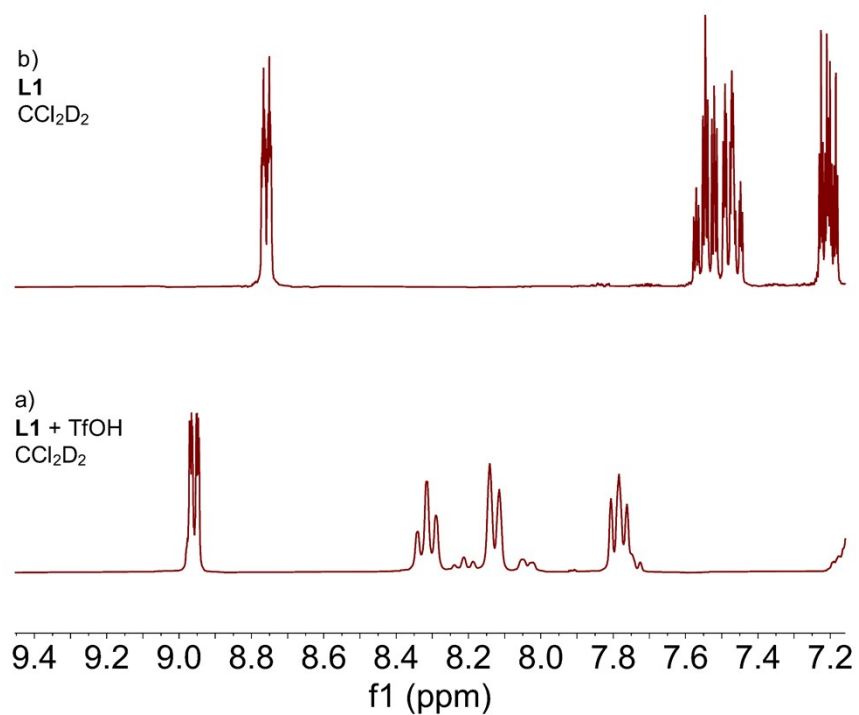
Figure SI-18   Selected region of the ¹H-NMR spectrum of the **L1** ligand in CD_2Cl_2/CF_3SO_3H (a) at rt and ap in comparison to the free ligand in CCl_2D_2 without the acid (b).
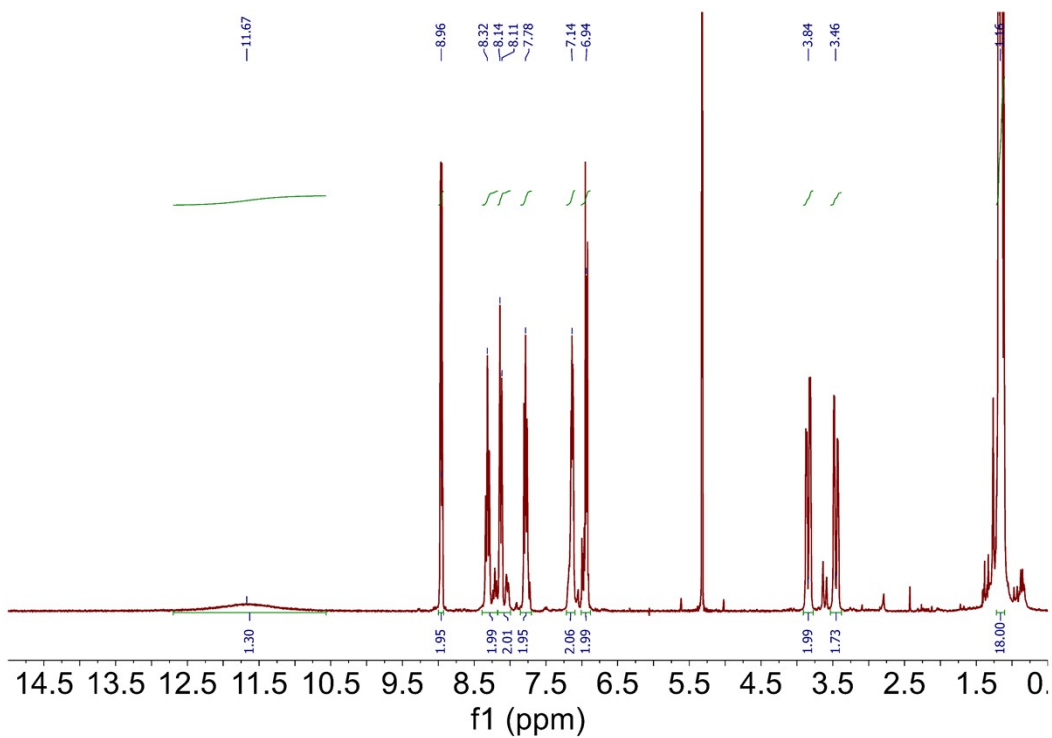
Figure SI-19   Selected region of the ¹H-NMR spectrum of the **L1** ligand in CD_2Cl_2/CF_3SO_3H (a) at rt.
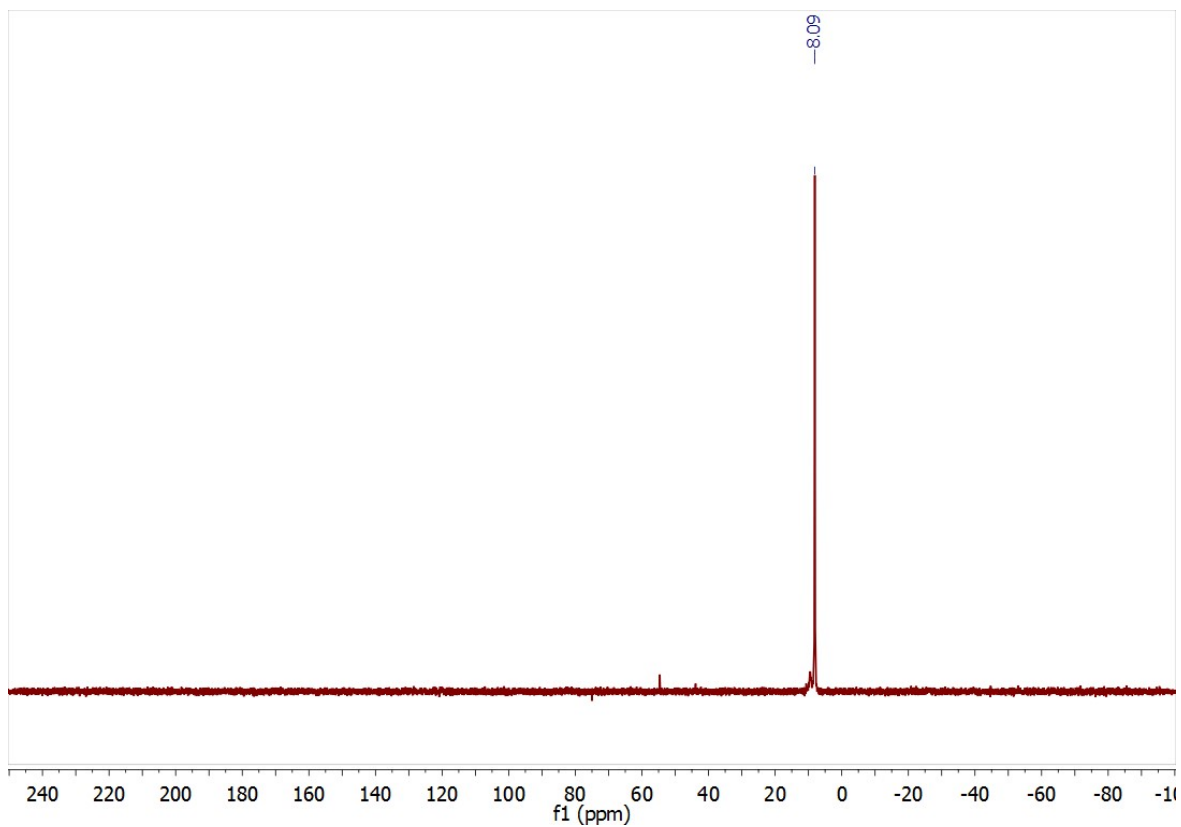
Figure SI-20   ³¹P{¹H}-NMR spectrum of the **L1** ligand in CD_2Cl_2/CF_3SO_3H at rt and ap.

—8.10
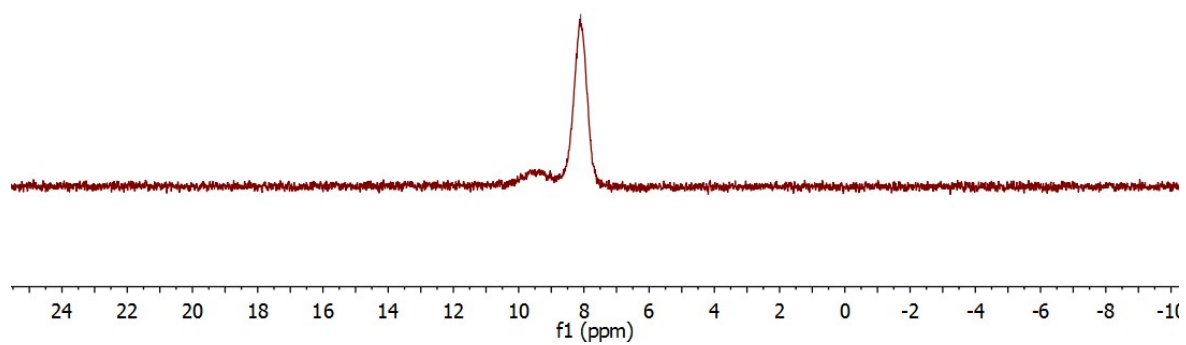
Figure SI-21 Proton-coupled ^{31}P-NMR spectrum of the **L1** ligand in CD$_2$Cl$_2$/CF$_3$SO$_3$H at rt and ap. Only the relevant part of the spectrum is shown.

In a separate variable temperature (VT) ^{1}H-NMR experiment for **L1**/2TfOH we found that the position and linewith of the signal for pyridinium protons shows variations and depend on the temperature (Fig. SI-22). With longer relaxation times, it was observed that the relative integral value of the Pyr-H$^+$ signal at 11.6 (297 K) and 14.8 ppm (213 K) reaches ≈1:1 compared to the adjacent proton of the pyridyl ring at 8.96 ppm. The signal of the pyridinium proton of commercial [C_6H_5NH][OT_f] lies at 15.2 ppm and shows a smaller integral value when measured with standard relaxation times (Fig. SI-23).
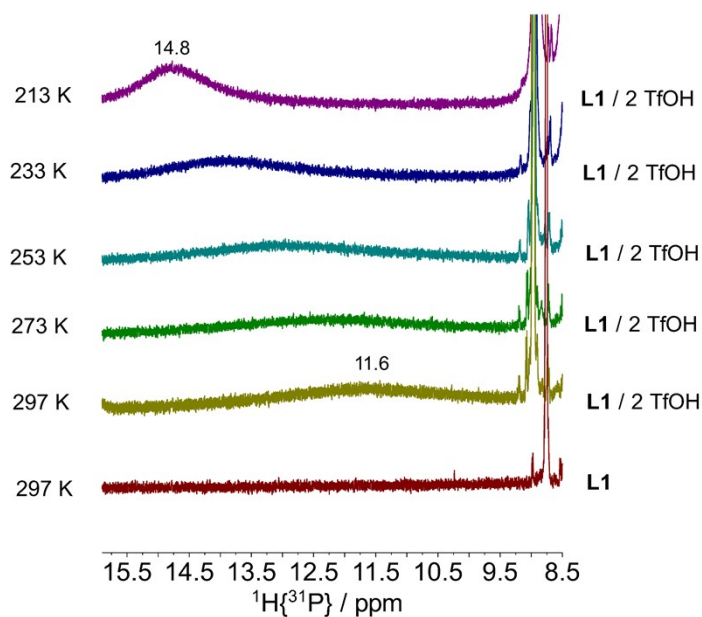
Figure SI-22   Selected region of a VT ^{1}H{^{31}P}-NMR experiment of the **L1** ligand in CD_2Cl_2/CF_3SO_3H.
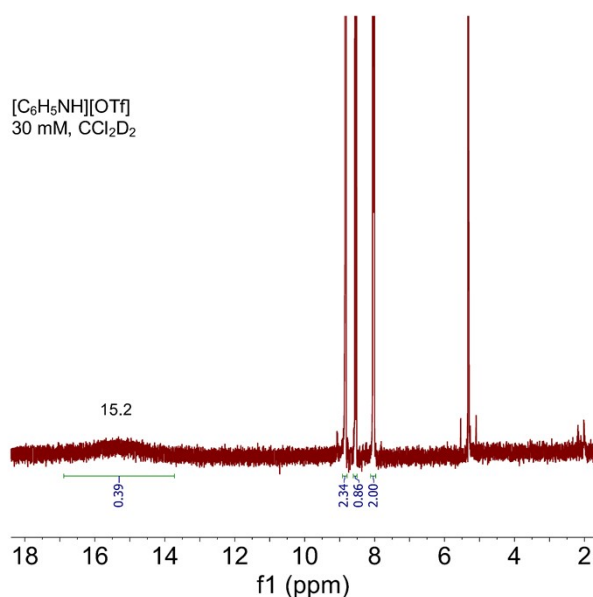
Figure SI-23 ^{1}H-NMR spectrum of [C_6H_5][OTf] in CD_2Cl_2 at RT.

<u>Phosphine **L2** / CF$_3$SO$_3$H</u>

^{1}H NMR (300 MHz, dichloromethane-d_2) δ 8.91 (m, 2H), 8.06 (t, J = 7.73 Hz, 2H), 7.91 (dd, J = 7.63 Hz, J = 3.87 Hz, 2H), 7.66 (m, 2H), 4.45 (m, 2H), 4.36 (m, 2H), 4.32 (m, 2H), 4.21 (m, 2H), 1.05 (d, ^{3}J$_{H,P}$ = 13.76 Hz, 18H).
^{31}P NMR (122 MHz, dichloromethane-d_2) δ 9.13 (s).
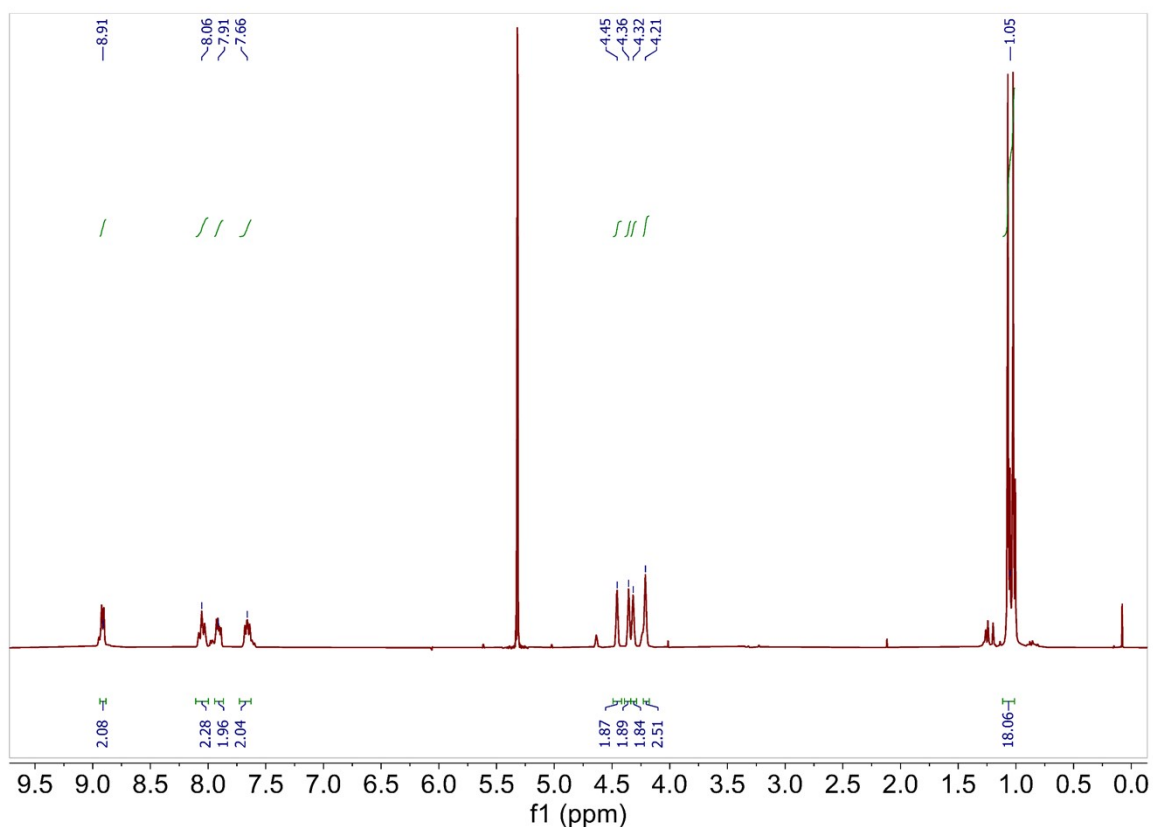
Figure SI-24 ^{1}H-NMR spectrum of the **L2** ligand in CD$_2$Cl$_2$/CF$_3$SO$_3$H at rt and ap.
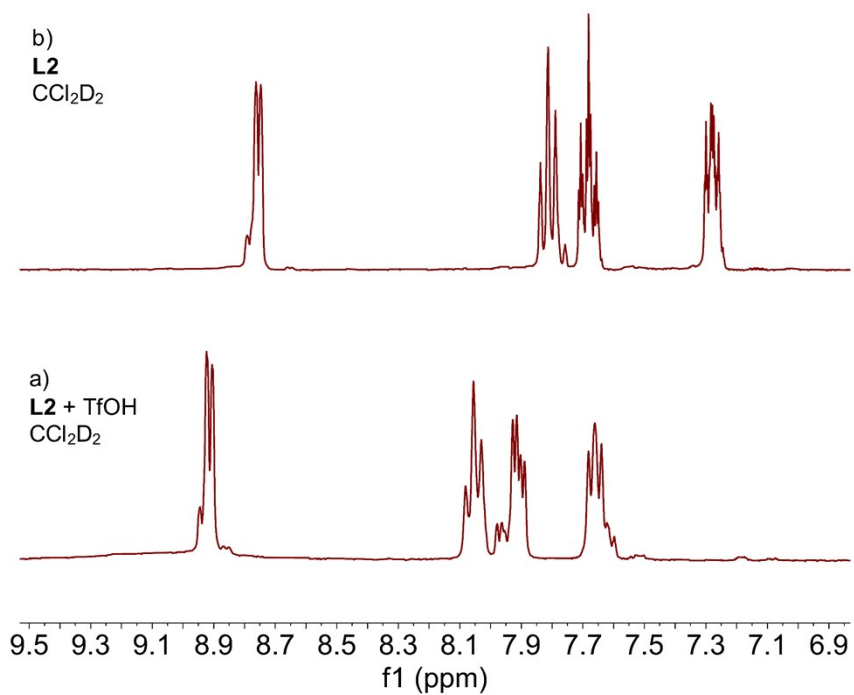
Figure SI-25   Selected region of the ^{1}H-NMR spectrum of the **L2** ligand in CD_2Cl_2/CF_3SO_3H (a) at rt and ap in comparison to the free ligand in CCl_2D_2 without the acid (b).
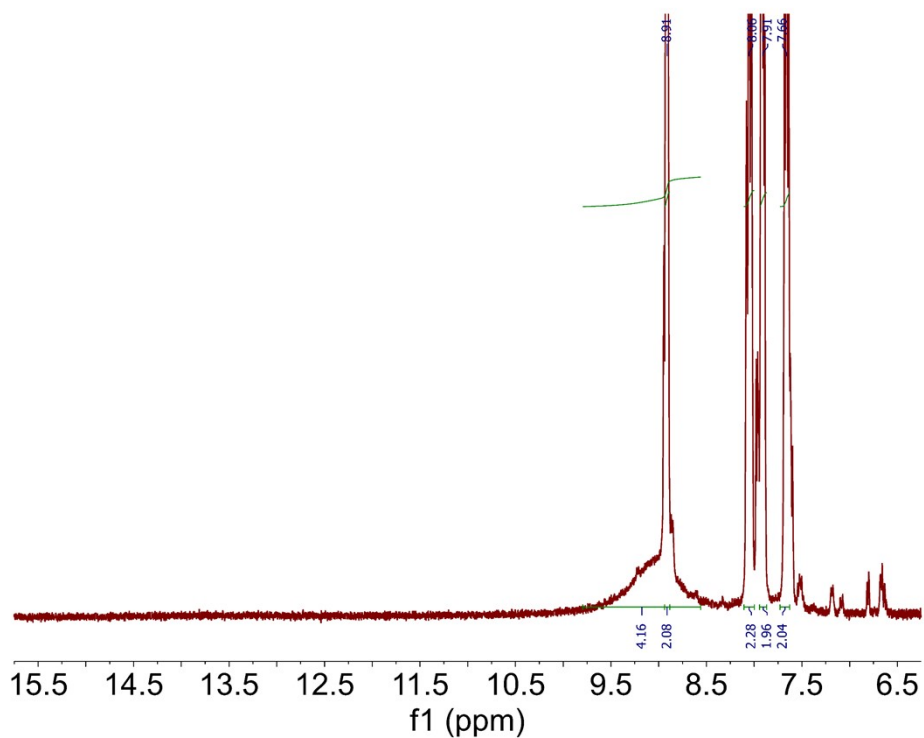
Figure SI-26   Selected region of the ^{1}H-NMR spectrum of the **L2** ligand in CD_2Cl_2/CF_3SO_3H (a) at rt and ap. The intengral ration for signals at ≈9.0 ppm and 8.91 ppm is nearly 1:1. The entire integral between 8.5 -9.6 ppm is 4.16, whereas the integral for the signal at 8.91 ppm is 2.08.
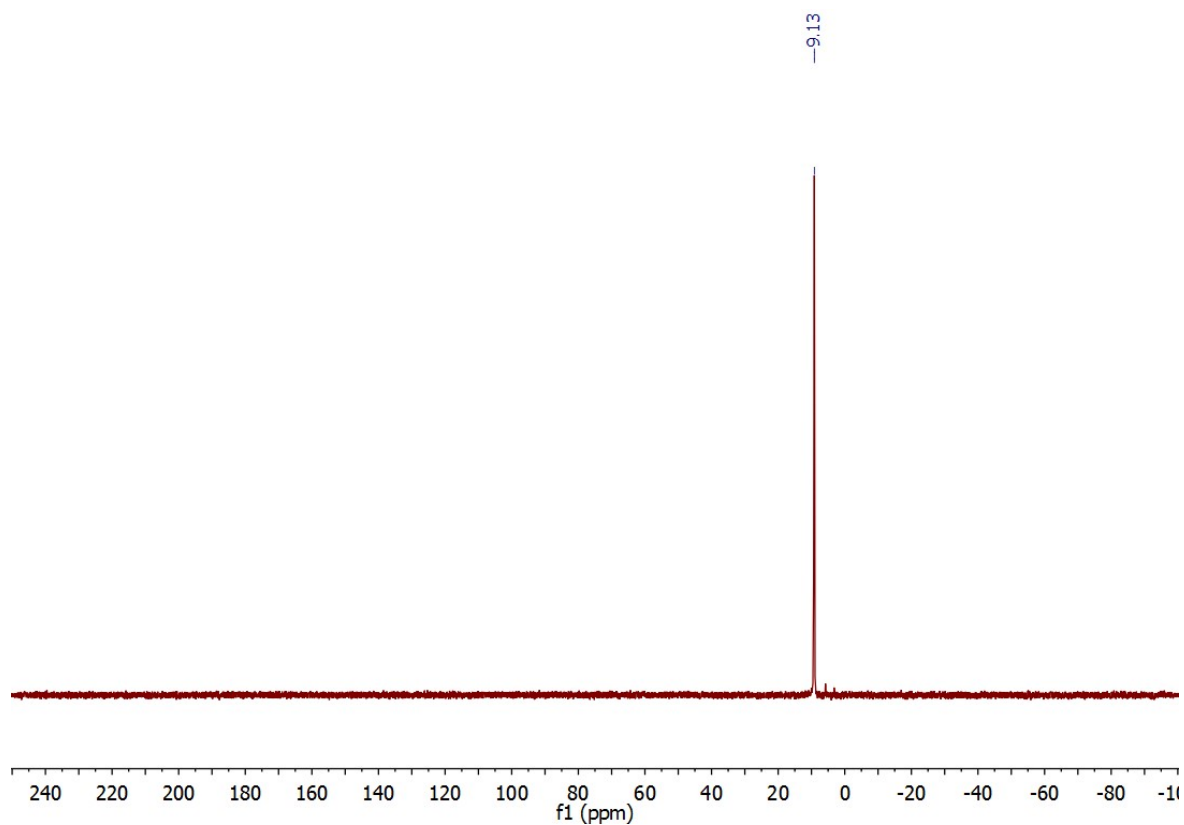
Figure SI-27 $^{31}P\{^1H\}$-NMR spectrum of the **L2** ligand in CD_2Cl_2/CF_3SO_3H at rt and ap.
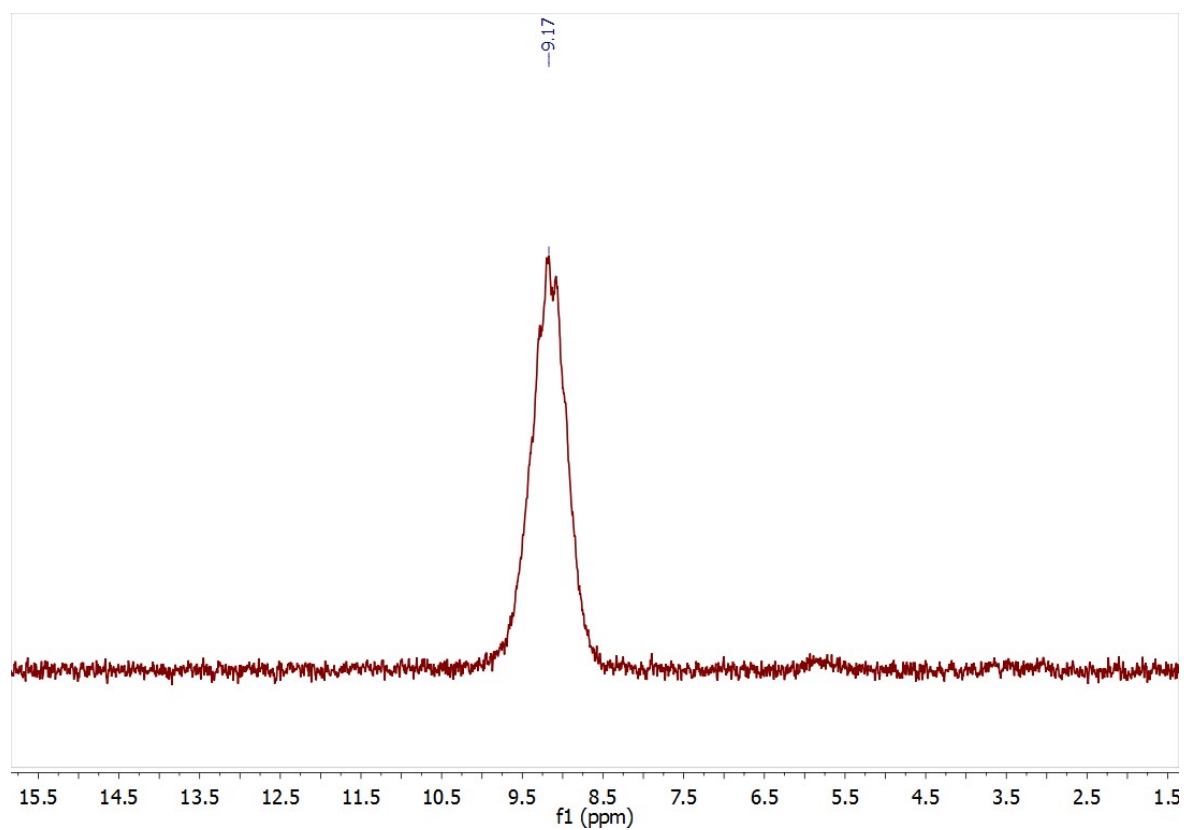
Figure SI-28 Proton-coupled ^{31}P-NMR spectrum of the **L2** ligand in CD_2Cl_2/CF_3SO_3H at rt and ap. Only the relevant part of the spectrum is shown.

Protonated phosphine **L3** / CF$_3$SO$_3$H

^{1}H NMR (300 MHz, dichloromethane-d_2) δ 7.57 – 7.40 (m, 4H, Ar-*H*), 5.9 (dt, $^1J_{H,P}$ = 454Hz, $^3J_{H,H}$ = 5.6 Hz, 2H, P-*H*), 3.86 (dd, $^2J_{H,P}$ = 13.7 Hz, $^3J_{H,H}$ = 5.6 Hz, 4H, Ar-C*H*$_2$-P), 1.48 (d, $^3J_{H,P}$ = 17.2 Hz, 36H, *t*Bu-*H*).
^{31}P NMR (122 MHz, dichloromethane-d_2) δ 51.52 (dm, $^1J_{H,P}$ = 454 Hz).
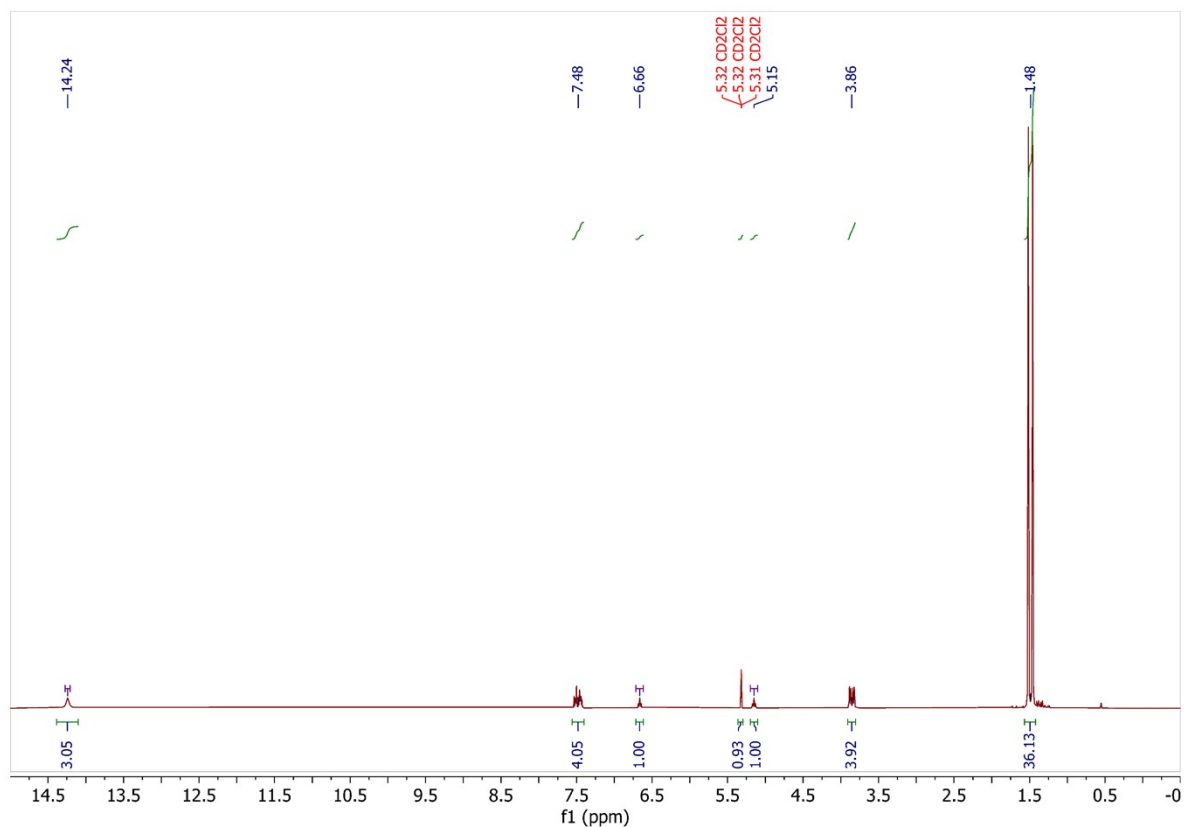
Figure SI-29 ^{1}H-NMR spectrum of the **L3** ligand in CD$_2$Cl$_2$/CF$_3$SO$_3$H at rt and ap.
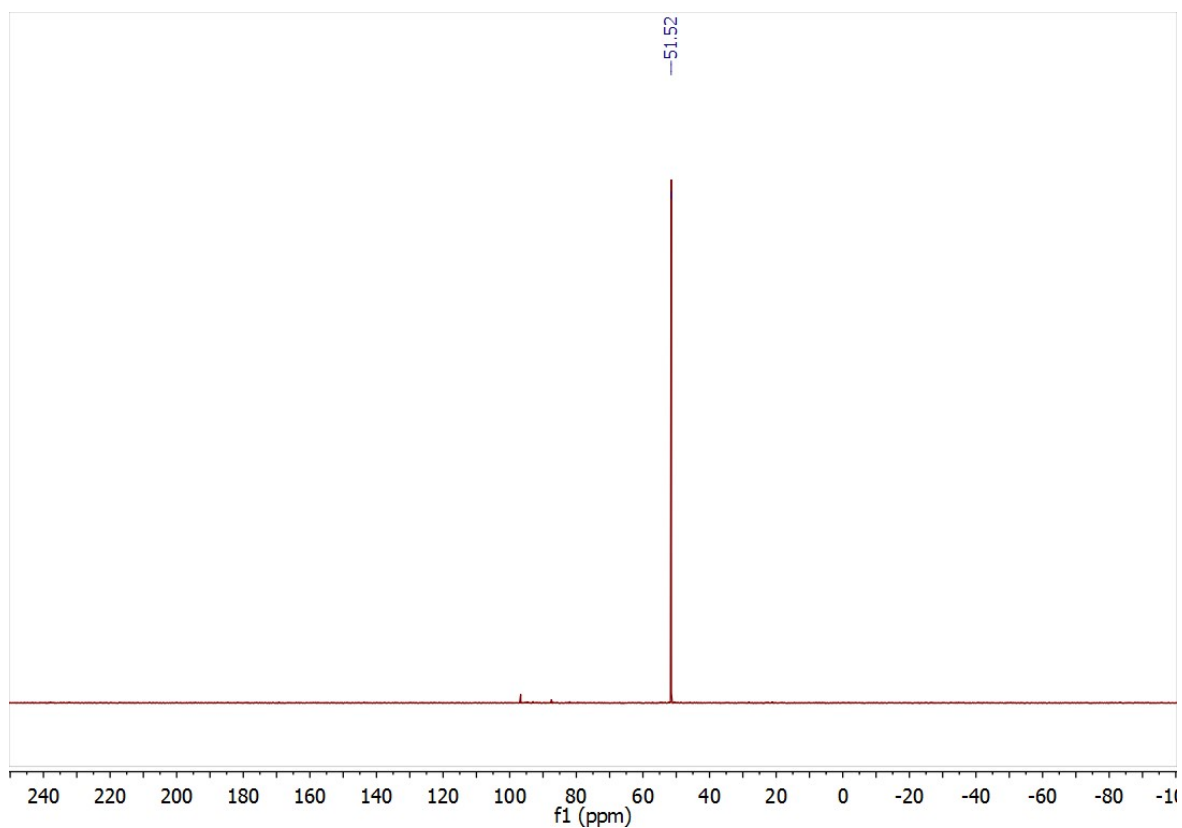
Figure SI-30 $^{31}P\{^1H\}$-NMR spectrum of the **L3** in CD_2Cl_2/CF_3SO_3H at rt and ap.
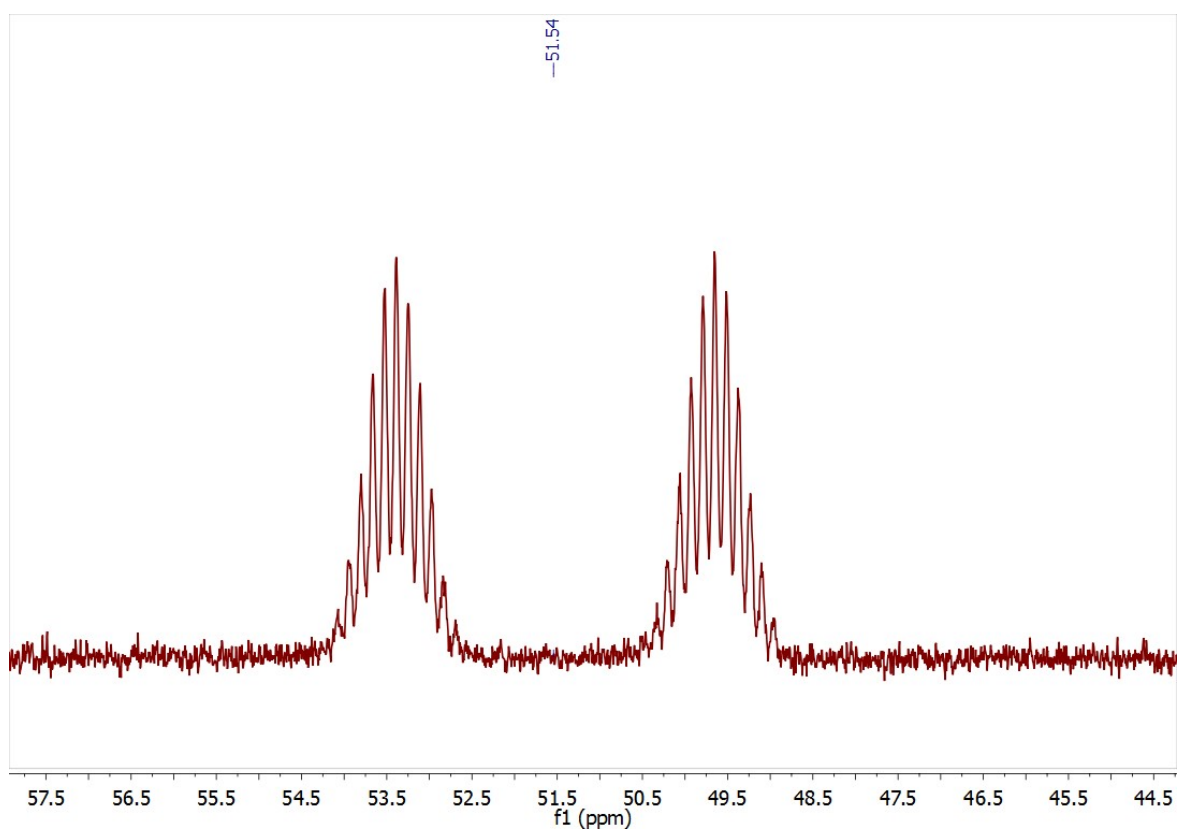
Figure SI-31 Proton coupled ^{31}P-NMR spectrum of the **L3** Ligand in CD_2Cl_2/CF_3SO_3H at rt and ap. The spectrum is scaled to show the signal of interest only.

SI-F: NMR-Characterization of synthesized [(P∩P)Pd(dba)] complexes (P∩P = **L1**, **L2**, **L3**)

$$[Pd_2(dba)_3] + 2\ P\cap P \xrightarrow[- dba]{THF} 2\ X\text{—}Pd(dba)$$

L1 X_1, R = 2-pyridyl
L2 X_2, R = 2-pyridyl
L3 X_1, R = ^tBu

P∩P X_1 X_2
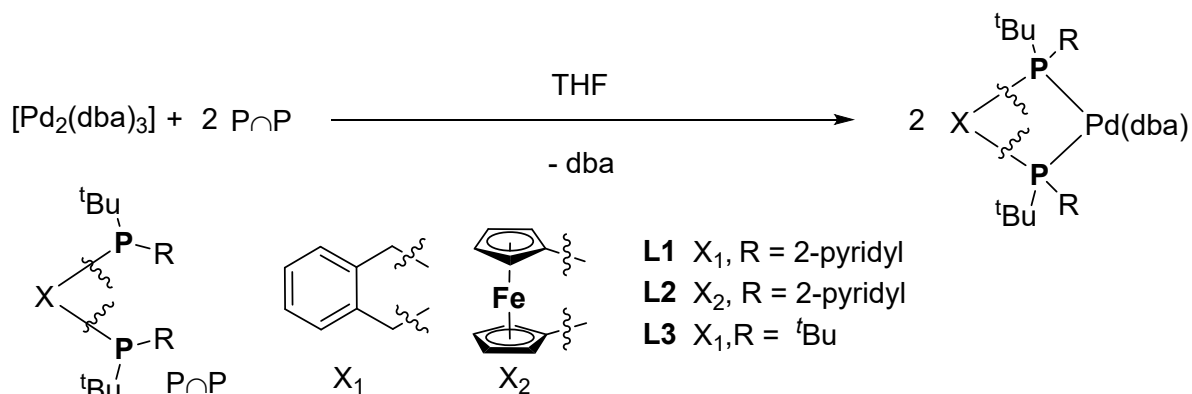
Preparation[7]

183.44 mg tris(dibenzylideneacetone)dipalladium(0) ([Pd$_2$(dba)$_3$], 0.2 mmol, 1 equivalent) and 2 equivalents of diphosphine ligand (**L1**, **L2**, **L3** 0.4 mmol) were dissolved in 20 mL tetrahydrofuran (THF) in a Schlenk flask under argon. The deep purple color of the resulting solution changed to bright orange after stirring for 2 h at room temperature. After stirring for additional 16 h, the reaction solution was fine-filtrated to remove insoluble parts (palladium black) and the solvent was removed under reduced pressure. The obtained reddish sticky gum was washed several times with heptane by using an ultrasonic bath.

[(**L1**)Pd(dba)]

orange solid, 60 % yield

³¹P{¹H} NMR (122 MHz, dichloromethane-d_2) δ 39.6 (s), 35.4 (s).
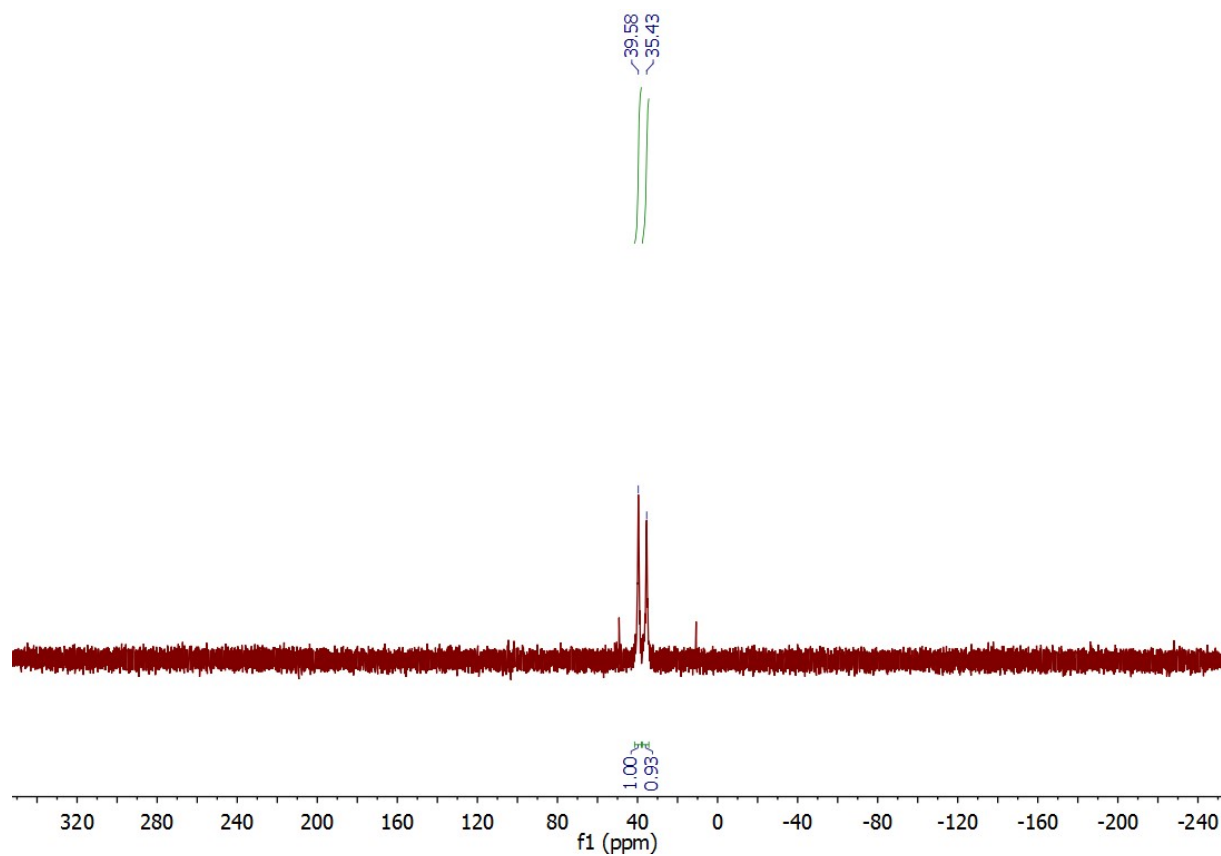
Figure SI-32   ³¹P{¹H}-NMR spectrum of [(**L1**)Pd(dba)] in CD_2Cl_2 at rt.

[(**L2**)Pd(dba)]

yellow solid, 70 % yield

^{31}P{^{1}H} NMR (122 MHz, dichloromethane-d_2) δ 46.6 (s), 44.8 (s).
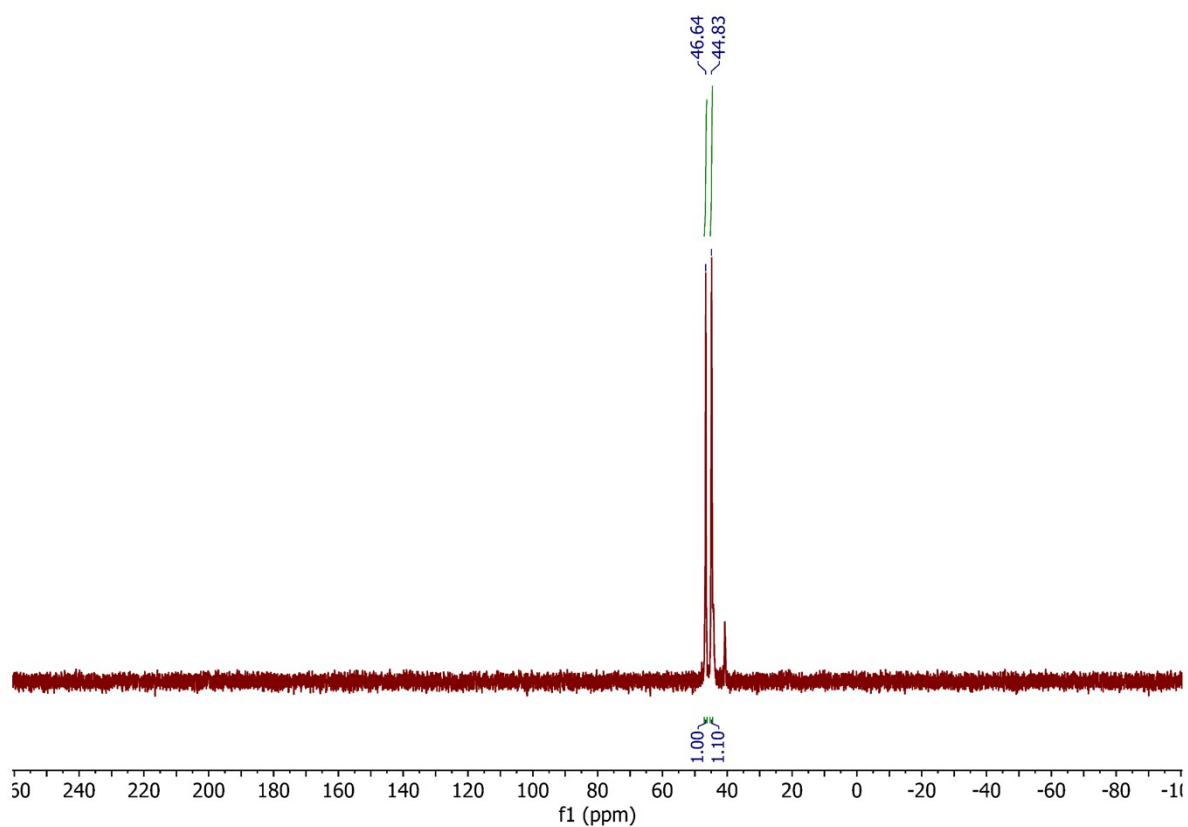
Figure SI-33 ^{31}P{^{1}H}-NMR spectrum of [(**L2**)Pd(dba)] in CD$_2$Cl$_2$ at rt.

[(**L3**)Pd(dba)]

yellow solid, 67 % yield

^{31}P{^{1}H} NMR (122 MHz, dichloromethane-d_2) δ 38.2 (s), 33.1 (s).
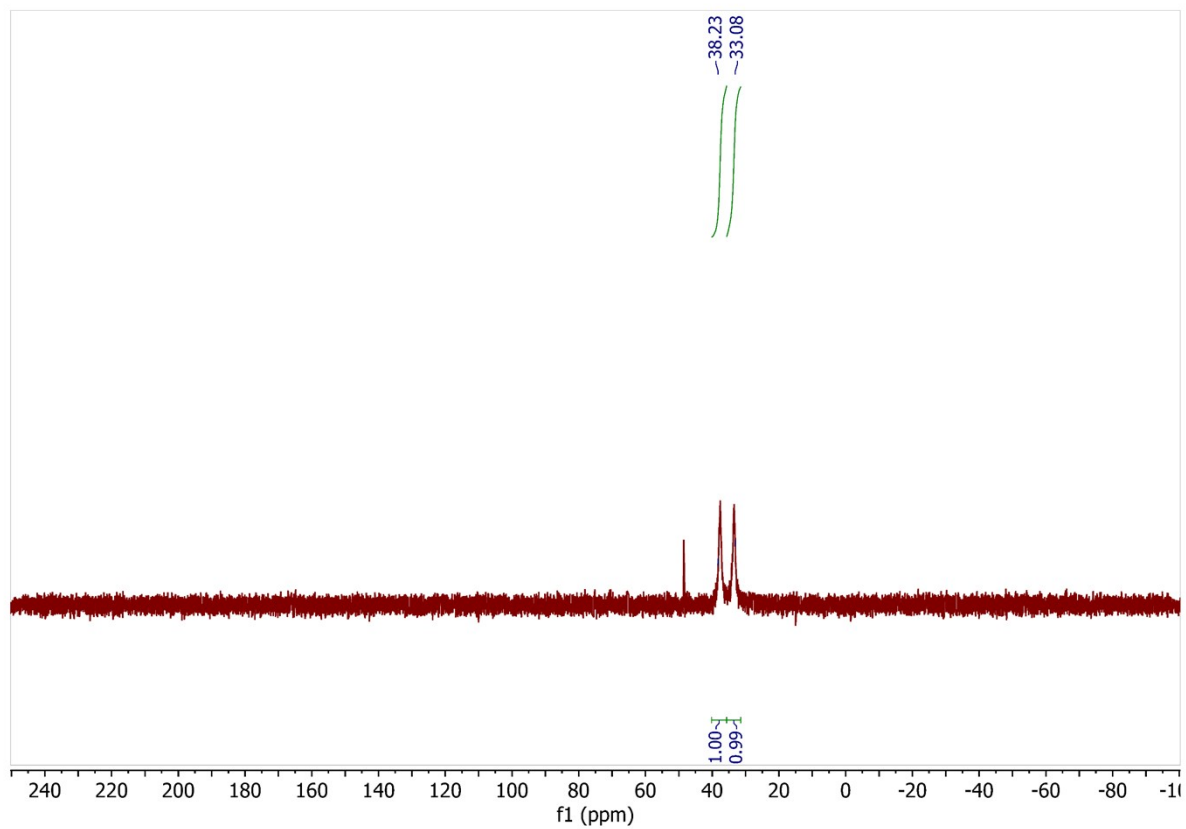
Figure SI-34 ^{31}P{^{1}H}-NMR spectrum of [(**L3**)Pd(dba)] in CD$_2$Cl$_2$ at rt.

SI-G: Treatment of [(P∩P)Pd(dba)] with CF_3SO_3H in the presence of benzochinone in methanol (P∩P = **L1**, **L2**, **L3**)

General experimental procedure

MeOH (15 V-% MeOH-d_4)

+ 1,4-benzoquinone 2 - 5 equiv.
+ CF_3SO_3H 2 - 5 equiv.

– dba

(L1) X_1
(L2) X_2

X_1 X_2

$CF_3SO_3^-$

(L1) X_1
(L2) X_2

MeOH (15 V-% MeOH-d_4)

+ 1,4-benzoquinone 2 equiv.
+ CF_3SO_3H 5 equiv.

– dba

(L3) X_1

X_1

$CF_3SO_3^-$

(L3) X_1
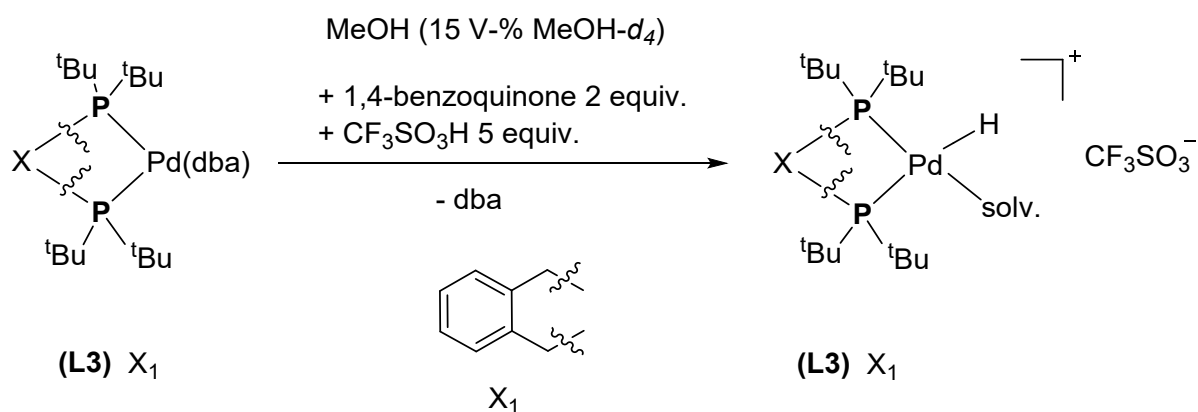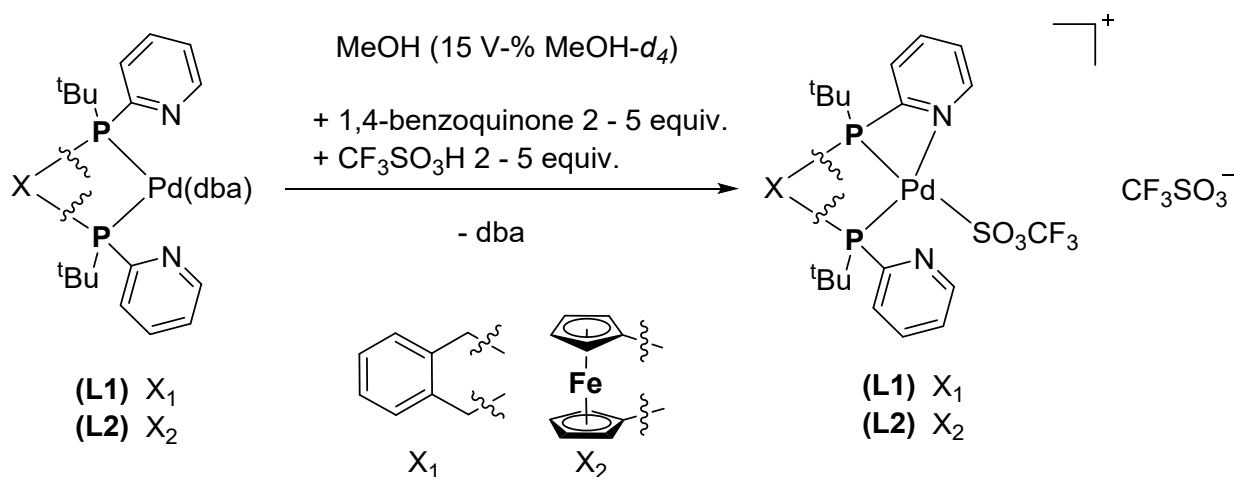
The samples were prepared starting from the corresponding [(L∩L)Pd(dba)] complexes (0.03 mmol) that were weighed into a 5 mL Schlenk flask together with benzoquinone (6.5 – 16.25 mg, 0.06 – 0.15 mmol) and dissolved in 0.5 mL of the desired NMR solvent under argon. A second solution was prepared containing the acid (0.06 - 0.15 mmol) and 0.5 mL of the NMR solvent. The acid was then transferred into the stirred complex solution and the combined mixture left stirring for a few minutes. A J. Young NMR tube was prepared and charged with the solution, which was then NMR spectroscopically analyzed.

[(**L1**)Pd(O$_3$SCF$_3$)](O$_3$SCF$_3$)

T = 297 K

^{1}H NMR (400 MHz, methanol-d_4) Most signals broad, no further assignment done: δ 8.96, 8.64, 8.45, 8.26, 8.11, 7.95, 1.31 (d, ^{2}J(P,H) = 17.0 Hz, ^{t}Bu), 1.01 (d, ^{2}J(P,H) = 19.4 Hz, ^{t}Bu). Rest of the signals belong to the solvent CH$_3$OH and benzochinone. No signals for Pd hydride species detected.

^{31}P NMR (162 MHz, methanol-d_4) δ 36.22 (s), -5.24 (s).

T = 223 K

^{1}H NMR (400 MHz, methanol-d$_4$) Most signals broad, no further assignment done: δ 8.96, 8.69 – 8.61, 8.51, 8.44, 8.30, 8.10, 7.95, 1.29 (d, ^{2}J(P,H) = 16.6 Hz, ^{t}Bu), 0.96 (d, ^{2}J(P,H) = 19.4 Hz, ^{t}Bu). Rest of the signals belong to the solvent CH$_3$OH and benzochinone. No signals for Pd hydride species detected.

^{31}P NMR (162 MHz, methanol-d_4) δ 35.72 (d, ^{2}J(P,P) = 11.5 Hz), -6.40 (d, ^{2}J(P,P) = 11.5 Hz).
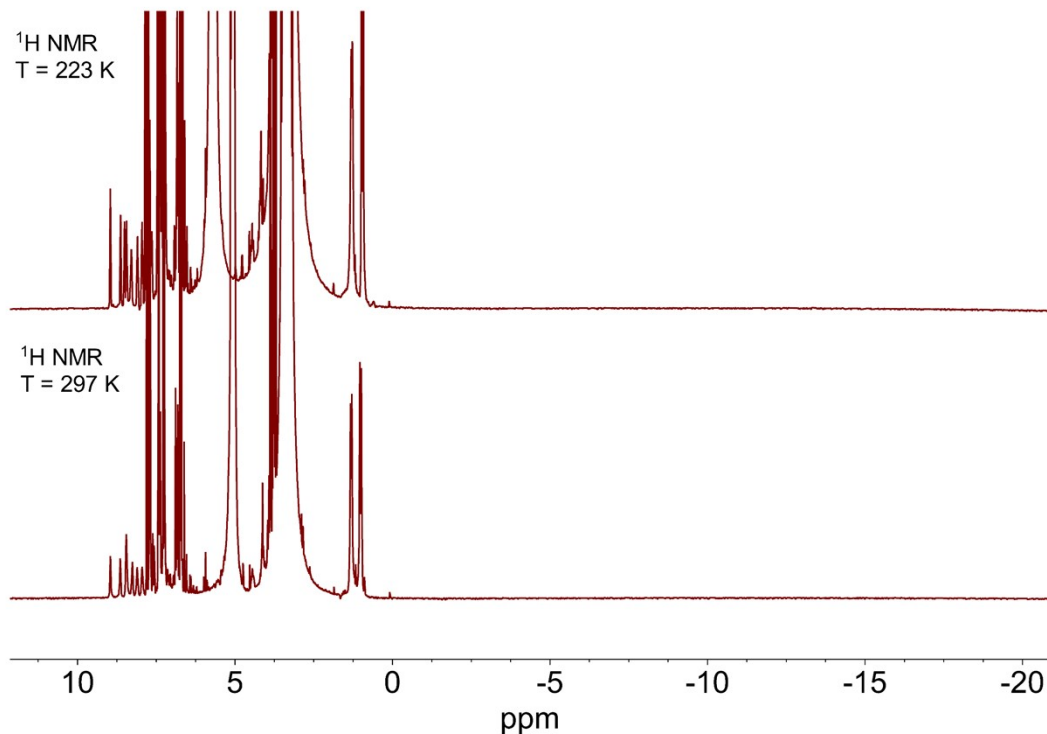
Figure SI-35 ^{1}H NMR spectra of [(**L1**)Pd(O$_3$SCF$_3$)](O$_3$SCF$_3$) in MeOH/MeOH-d$_4$ at 297 and 223 K.
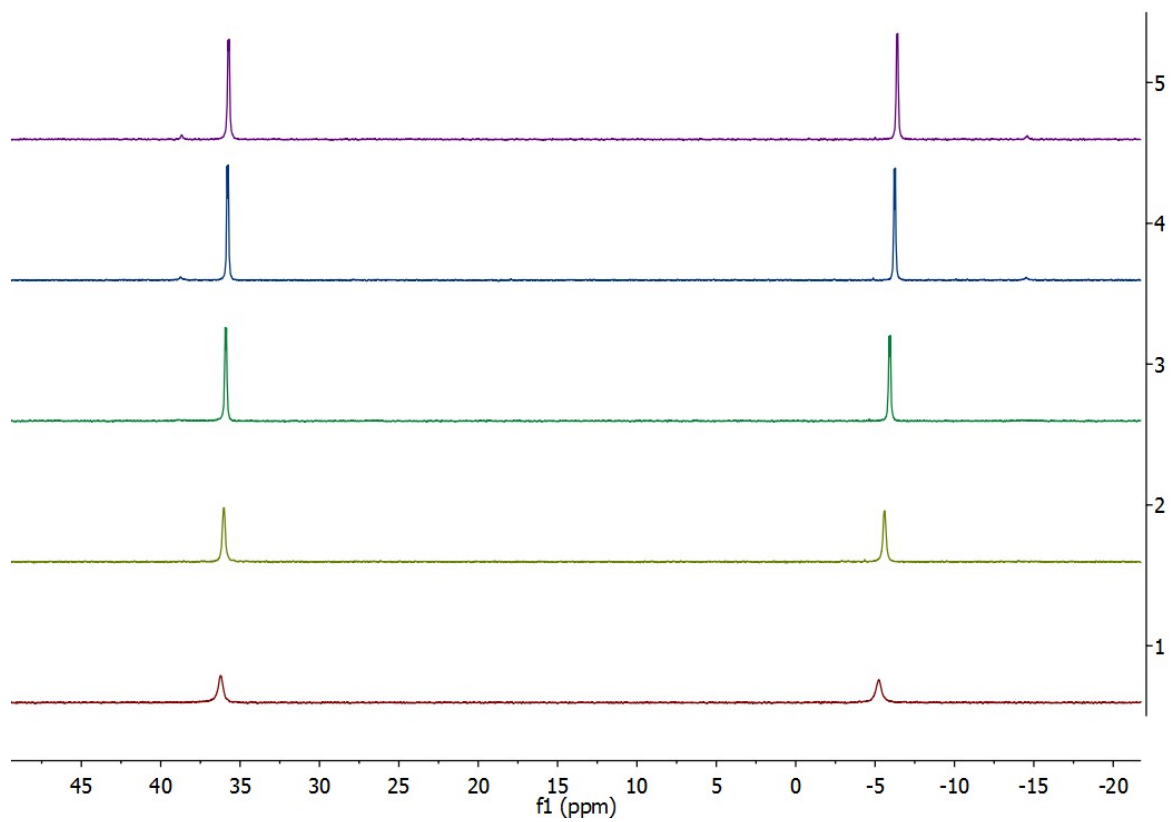
Figure SI-36 VT ^{31}P NMR spectra of [(**L1**)Pd(O$_3$SCF$_3$)](O$_3$SCF$_3$) in MeOH-d_4. [**1**] 293 K; [**2**] 273 K; [**3**] 253 K; [**4**] 233 K; [**5**] 223 K.

[(**L2**)Pd(O$_3$SCF$_3$)](O$_3$SCF$_3$)

T = 297 K
^{1}H NMR (400 MHz, methanol-d_4) Most signals broad, no further assignment done: δ 9.2 – 7.5 (pyridyl moiety, major/minor compound), 6.5 – 4.5 (ferrocenyl moiety, major/minor compound) 1.51 (^{t}Bu, minor), 0.92 (^{t}Bu, major). Rest of the signals belong to the solvent CH$_3$OH, pTSA, DBA and benzochinone.
No signals for Pd hydride species detected.
^{31}P NMR (162 MHz, methanol-d_4)
Major compound: δ 59.9 (s), -0.6 (s).
Minor compound: δ 21.5 (s)
Unknown further signals: δ -23.9 (s), -26.7 (s)

T 263 K
^{1}H NMR (400 MHz, methanol-d_4) No further assignment done.
^{31}P{^{1}H} NMR (162 MHz, methanol-d_4)
Major compound: δ 59.56 (s), -1.57 (s).
Minor compound: δ 21.72 (S)
Unknown further signals: δ -24.27 (s), -27.20 (s)

T 223 K
^{1}H NMR (400 MHz, methanol-d_4) No further assignment done.
No signals for Pd hydride species detected.
^{31}P{^{1}H} NMR (162 MHz, methanol-d_4)
Major compound: δ 58.94 (d, ^{2}J(P,P) = 27.0 Hz), -2.13 (d, ^{2}J(P,P) = 27.0 Hz).
Unknown further signals: δ -27.94 (s)
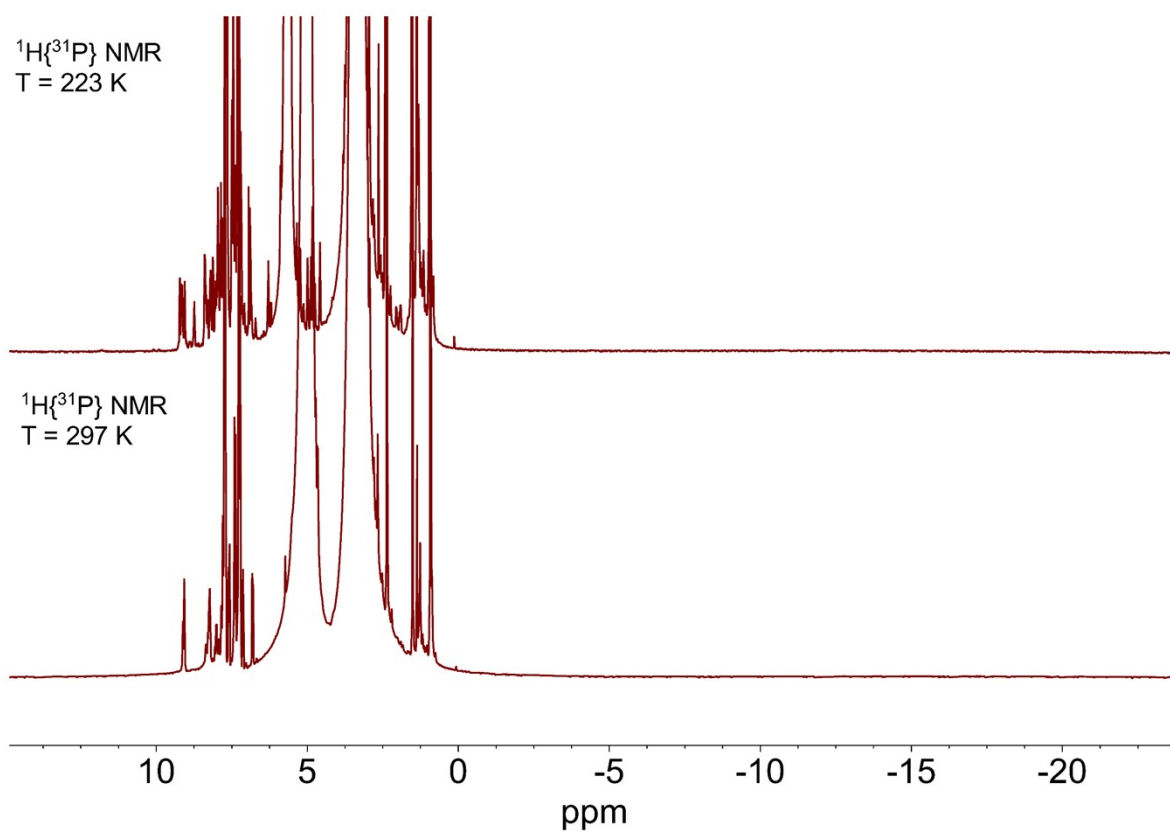
Figure SI-37 ^{1}H NMR spectra of [(**L2**)Pd(O$_3$SCF$_3$)](O$_3$SCF$_3$) in MeOH/MeOH-d$_4$ at 297 and 223 K.
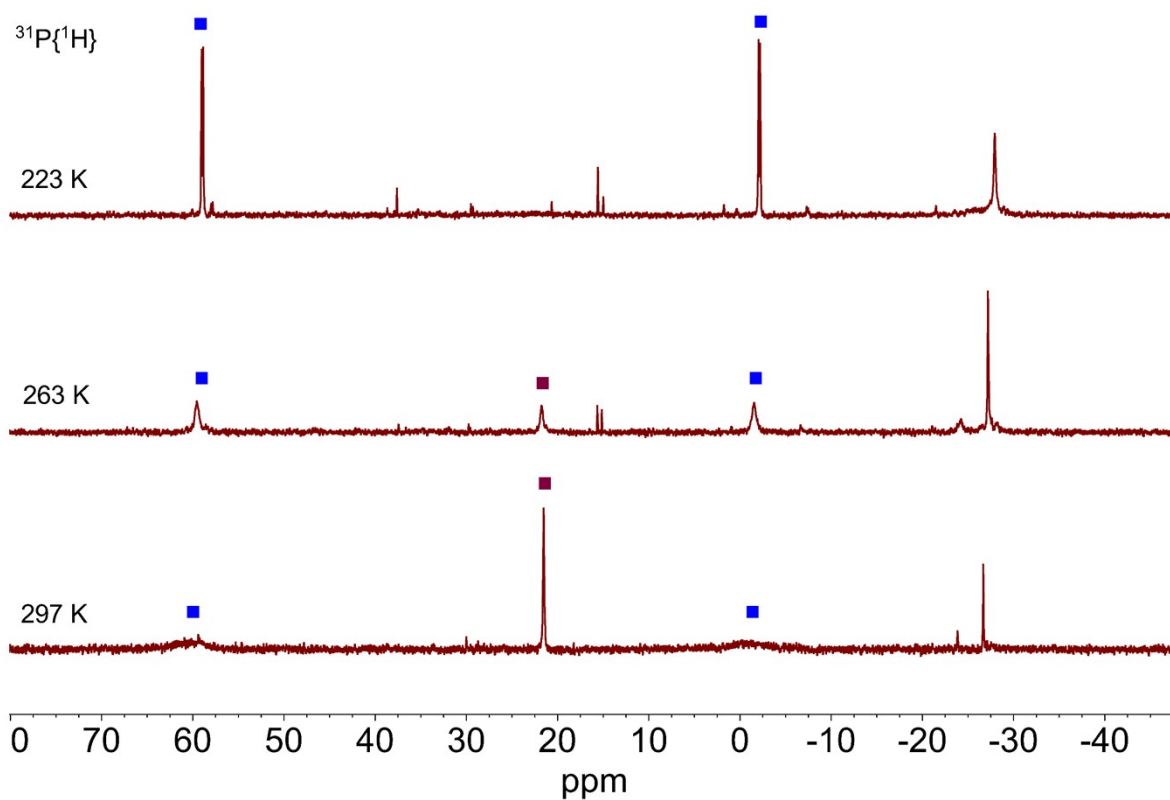
Figure SI-38 ^{31}P{^{1}H} NMR spectra of [(**L2**)Pd(O$_3$SCF$_3$)](O$_3$SCF$_3$) in MeOH/MeOH-d$_4$ at 297, 263 and 223 K.

[(**L3**)Pd(H)(MeOH)](O$_3$SCF$_3$)

NMR yield: 42 % according to ^{31}P NMR

^{1}H NMR (300 MHz, methanol-d_4) δ -10.71 (dd, $^2J_{H,P}$(*trans*) = 182.6 Hz, $^2J_{H,P}$(*cis*) = 21.7 Hz).
^{31}P{^{1}H} NMR (122 MHz, methanol-d_4) δ 75.62 (d, $^2J_{P,P}$ = 17.1 Hz), 23.90 (d, $^2J_{P,P}$ = 17.1 Hz).

P,H-coupling not resolved in ^{31}P NMR.
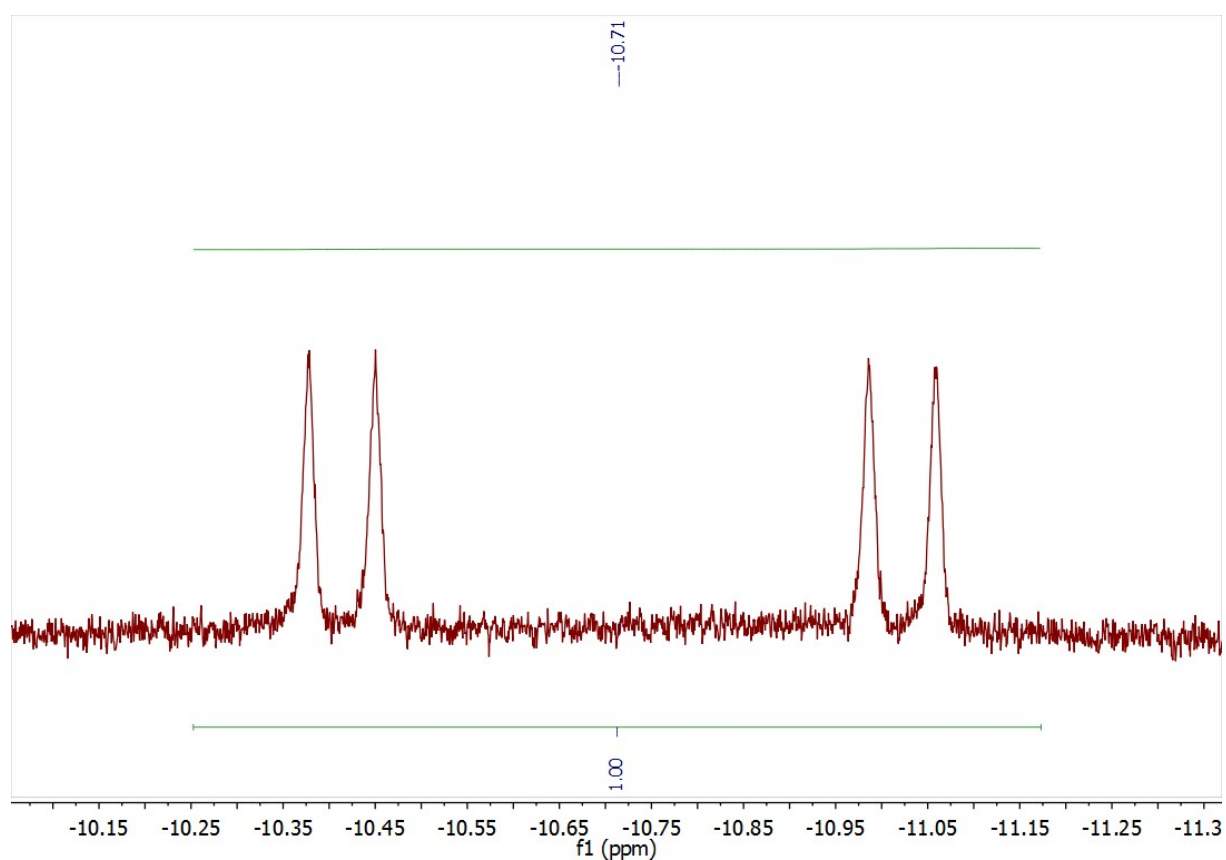
Figure SI-39 ^{1}H NMR spectrum of [(**L3**)Pd(H)(MeOH)](O$_3$SCF$_3$) in MeOH-d_4 at rt and ap. Only the hydride signal is displayed.
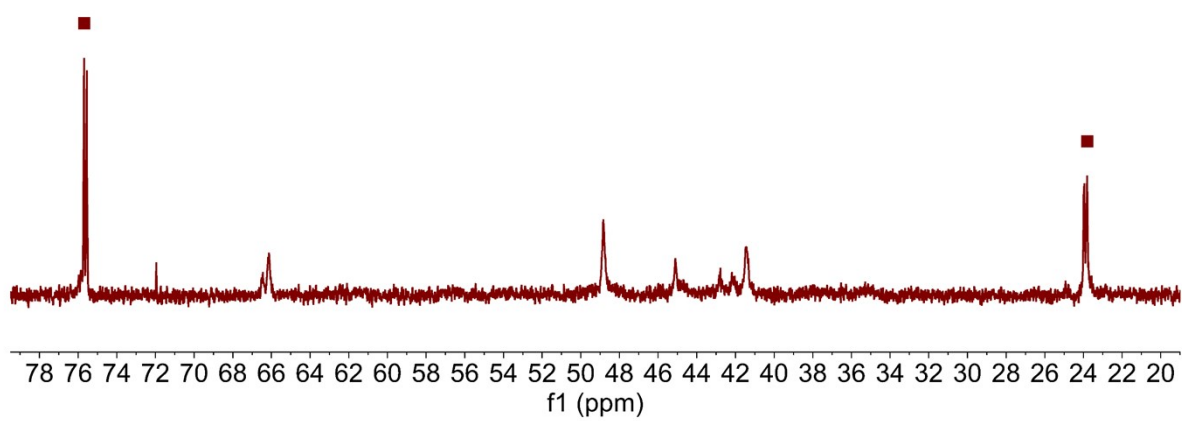
Figure SI-40 ^{31}P{^{1}H} NMR spectrum of [(**L3**)Pd(H)(MeOH)](O$_3$SCF$_3$) in MeOH-d_4 at rt and ap.

SI-H: Preparation and NMR-Characterization of sulfonate complexes of the type $[(P{\cap}PN)Pd(O_3SCF_3)](O_3SCF_3)$ ($P{\cap}P$ = **L1**, **L2**)
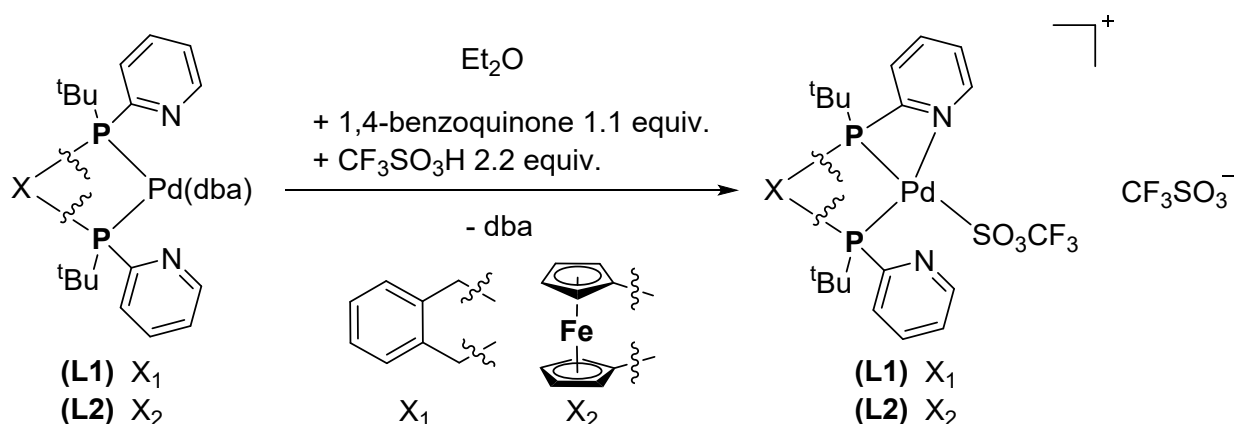
0.18 mmol of $[(P{\cap}P)Pd(dba)]$- complex (1 equivalent, 139.85 mg (**L1**), 154.24 mg (**L2**)) and 1.1 equivalents of 1,4-benzoquinone (0.198 mmol, 21.4 mg) were dissolved in 15 mL diethylether (Et_2O) in a Schlenk flask under argon. In an additional Schlenk flask 2.2 equivalents of trifluoromethanesulfonic acid (0.59 mmol, 34.3 µL) were diluted with 5 mL of Et_2O. The obtained acid solution was added dropwise to the previous prepared solution. After combining the solutions, the color changed to dark green. The reaction mixture was stirred for 12 h while a yellow precipitate was formed that was filtered off and washed several times with Et_2O.

[(**L1**)Pd(O₃SCF₃)](O₃SCF₃)

yellowish powder, 50 % yield

¹H NMR (300 MHz, dichloromethane-d_2) d 9.00 – 8.93 (m, 1H, Py^1-H), 8.86 (d, J = 4.2 Hz, 1H, Py^2-H), 8.67 Hz (t, J = 6.5 Hz, 1H, Py^1-H), 8.50 (t, J = 6.8 Hz, 1H, Py^2-H), 8.30 (t, J = 7.7 Hz, 1H, Py^1-H), 8.10 – 8.02 (m, 1H, Py^2-H), 7.77 (t, J = 6.8 Hz, 1H, Py^1-H), 7.64 – 7.58 (m, 1H, Py^2-H), 7.55 (d, J = 7 Hz, 1H, Xy-H), 7.46 – 7.36 (m, 2H, Xy-H), 7.29 (t, J = 7.3 Hz, 1H, Xy-H), 4.40 (t, J = 16.1 Hz, 2H, Ar-CH^aH^b-P), 3.69 (dd, J = 15.2 Hz, J = 7.0 Hz, 1H, Ar-CH^aH^b-P), 3.57 (t, J = 13.2 Hz, 1H, Ar-CH^aH^b-P), 1.34 (d, J = 17.5 Hz, 9H, tBu^1-H), 1.05 (d, J = 19.4 Hz, 9H, tBu^2-H).

³¹P NMR (122 MHz, dichloromethane-d_2) δ 33.50 (d, $^2J_{P,P}$ = 11.8 Hz, 1P), -5.04 (d, $^2J_{P,P}$ = 11.8 Hz, 1P).

¹⁹F NMR (376 MHz, dichloromethane-d_2)) δ - 78.22 (s).

In the ^{1}H-NMR spectrum multiple impurities are visible. These impurities are: Diethylether (at δ 3.43 (q, 2H), 1.15 (t, 3H)) and 1,4-benzoquinone (at δ 6.67 (s)). The ratio of complex:BQ:Diethylether is ca. 4:1:1.
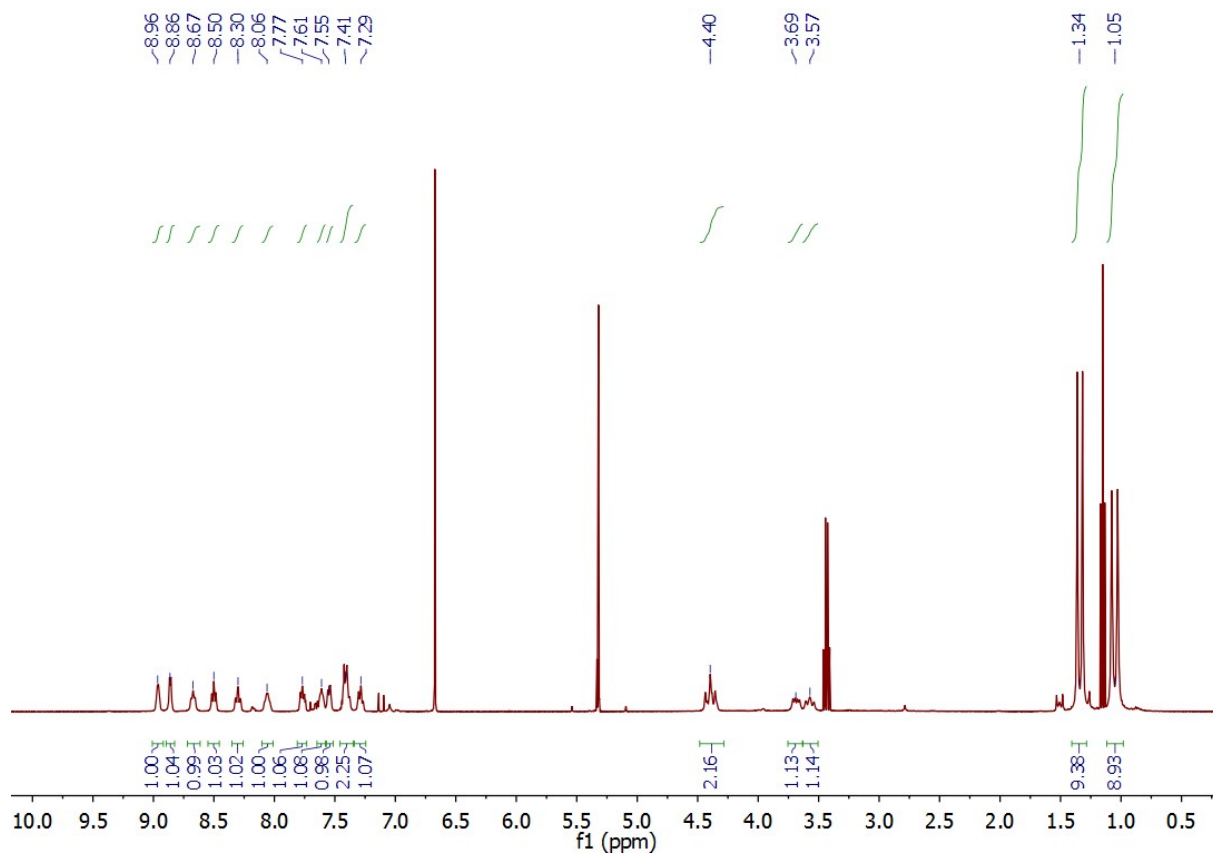
Figure SI-41 ^{1}H NMR spectrum of [(**L1**)Pd(O$_3$SCF$_3$)](O$_3$SCF$_3$) in DCM-d_2. Impurities are diethylether and benzoquinone.
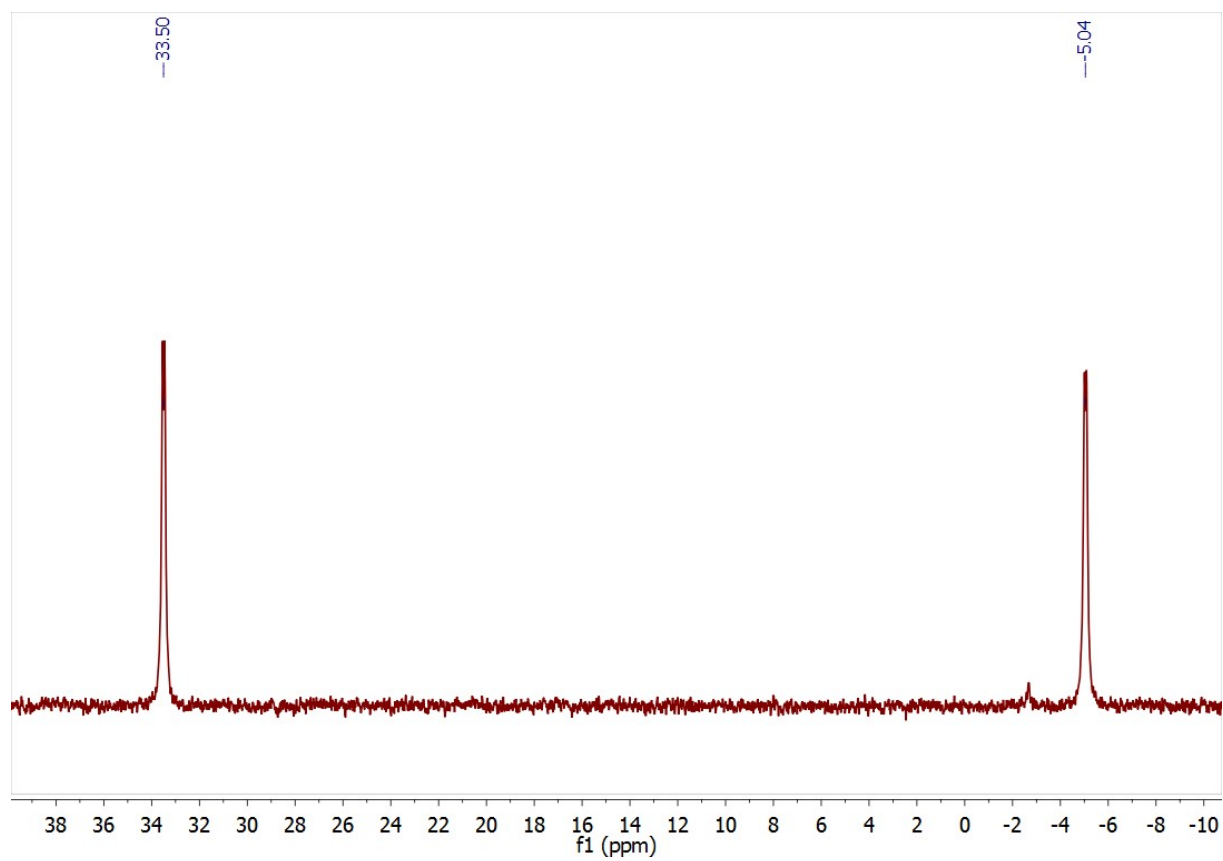
Figure SI-42 ^{31}P NMR spectrum of [(**L1**)Pd(O$_3$SCF$_3$)](O$_3$SCF$_3$) in CD$_2$Cl$_2$ at rt and ap.
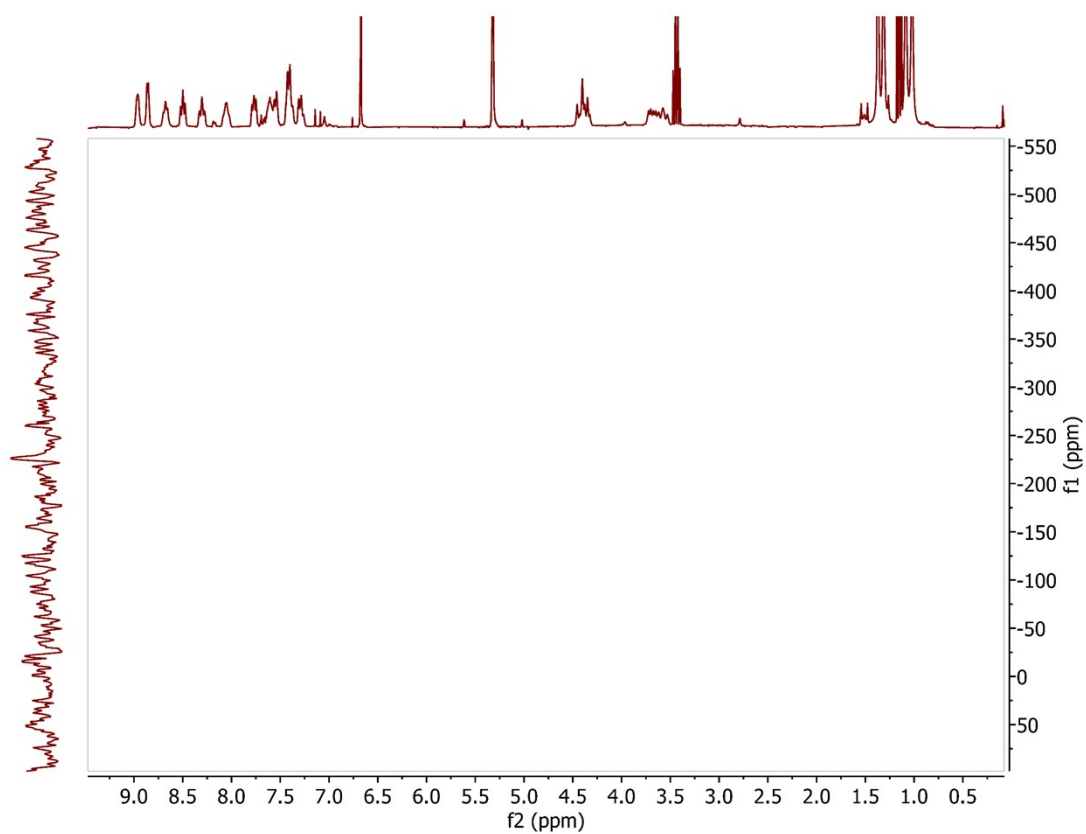
Figure SI-43 ^{1}H/^{15}N-HMBC NMR spectrum (300 MHz) of [(**L1**)Pd(O$_3$SCF$_3$)](O$_3$SCF$_3$) in CD$_2$Cl$_2$ at rt. Transfer delay 100 ms (J = 5 Hz). No signals assignable to a Py-N are visible. Neither changing the transfer delay to 71.4 ms (J = 7 Hz) nor lowering the temperature to −20 °C led to an improvement.
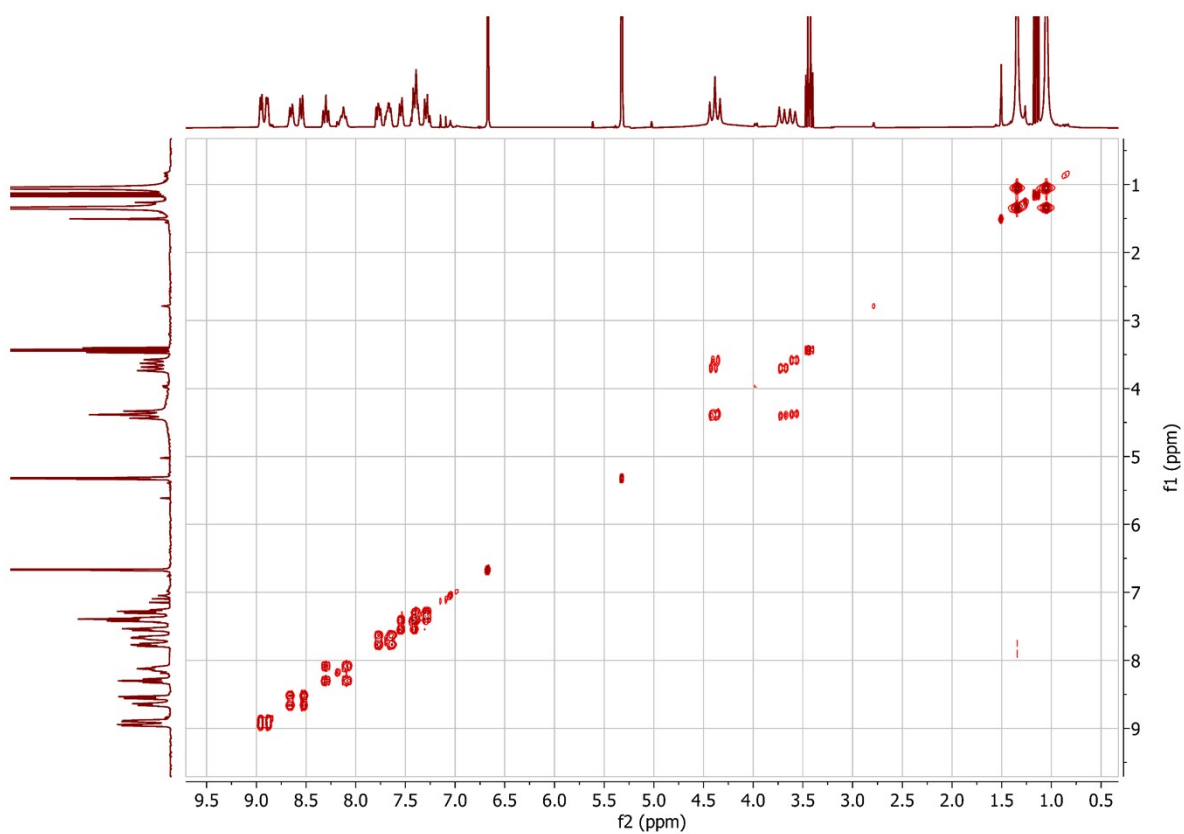
Figure SI-44 ^{1}H-^{1}H EXSY NMR spectrum (300 MHz) of [(**L1**)Pd(O$_3$SCF$_3$)](O$_3$SCF$_3$) in CD$_2$Cl$_2$ at rt. Short spin evolution times (0.3 s) were picked to show preferentially spin correlations due to chemical exchange rather than spatial correlations. The top trace (1D spectrum) is phosphorus-decoupled.
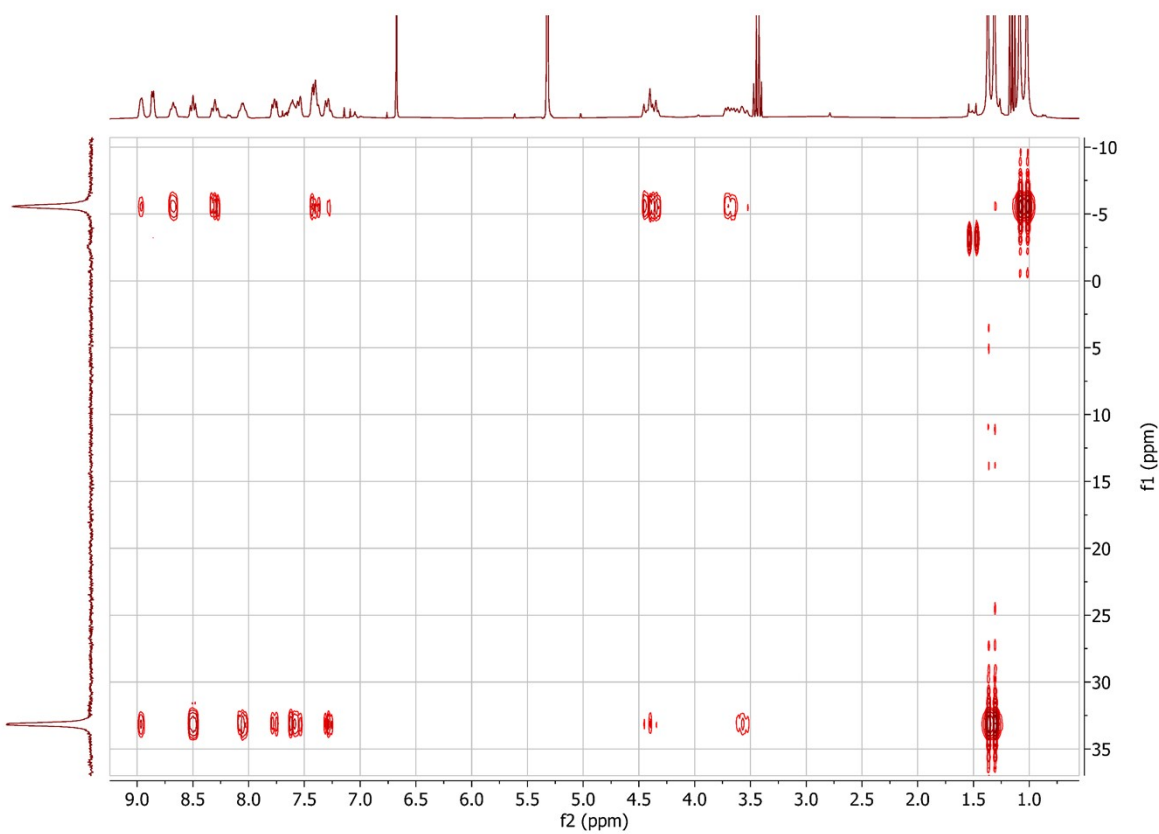
Figure SI- 45 ^{1}H/^{31}P-HMBC NMR spectrum (300 MHz) of [(**L1**)Pd(O$_3$SCF$_3$)](O$_3$SCF$_3$) in CD$_2$Cl$_2$ at rt. Transfer delay 67.6 ms. The top trace (1D spectrum) is phosphorus-coupled.

−78.22

110 80 50 20 -10 -40 -70 -100 -130 -160 -190 -220
f1 (ppm)
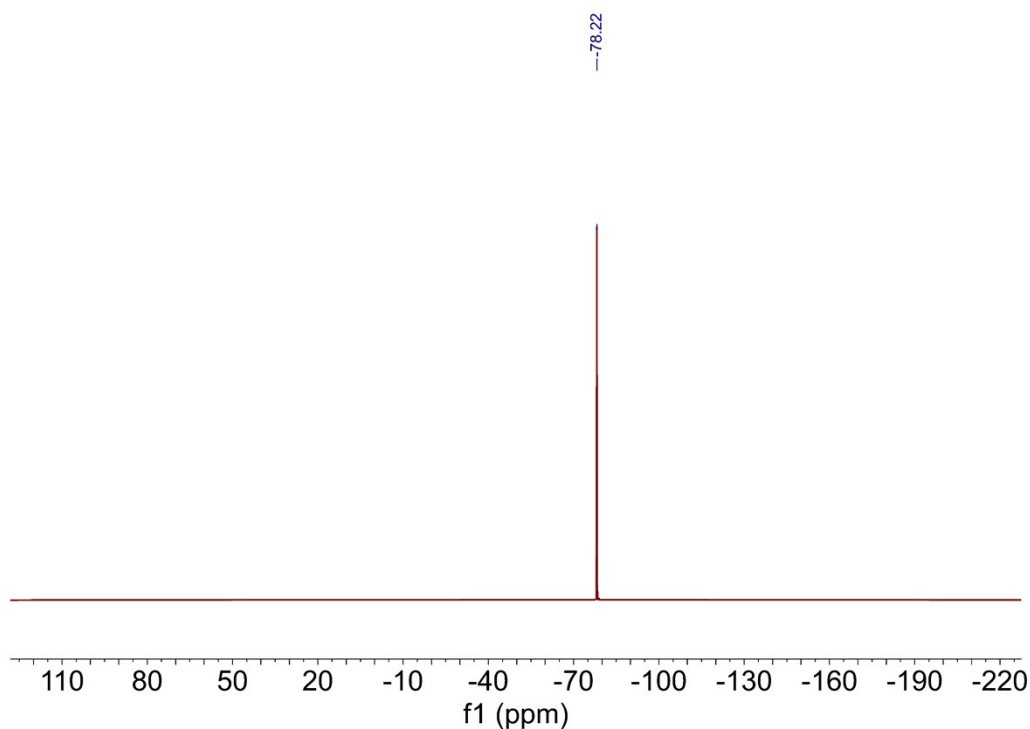
Figure SI-46 ^{19}F NMR spectrum (376 MHz) of [(**L1**)Pd(O$_3$SCF$_3$)](O$_3$SCF$_3$) in CD$_2$Cl$_2$ at rt.

[(L2)Pd(O$_3$SCF$_3$)](O$_3$SCF$_3$)

red powder, 54 % yield; mixture of two diastereomers in a 71:29 ratio

^{1}H NMR (300 MHz, dichloromethane-d_2, most signals broad, no further assignment done): δ 9.22, 9.02, 8.97, 8.33, 8.26, 7.88, 7.82, 7.66, 7.60, 6.68, 6.31, 6.05, 5.68, 5.42, 5.18, 4.93, 4.76, 4.73, 4.52, 1.54 (2 ^{t}Bu *minor*), 1.05 (d, $^2J_{P,H}$ = 17.4 Hz, 1 ^{t}Bu *major*), 0.97 (d, $^2J_{P,H}$ = 19.8 Hz, 1 ^{t}Bu *major*).
^{31}P NMR (122 MHz, dichloromethane-d_2): *Major* diastereoisomer: δ 59.82 (d, $^2J_{P,P}$ = 28.3 Hz, 1P), −1.52 (d, $^2J_{P,P}$ = 28.3 Hz, 1P). *Minor* diastereoisomer: δ 17.71 ppm (s).
^{19}F NMR (376 MHz, dichloromethane-d_2): δ -77.98 (s).
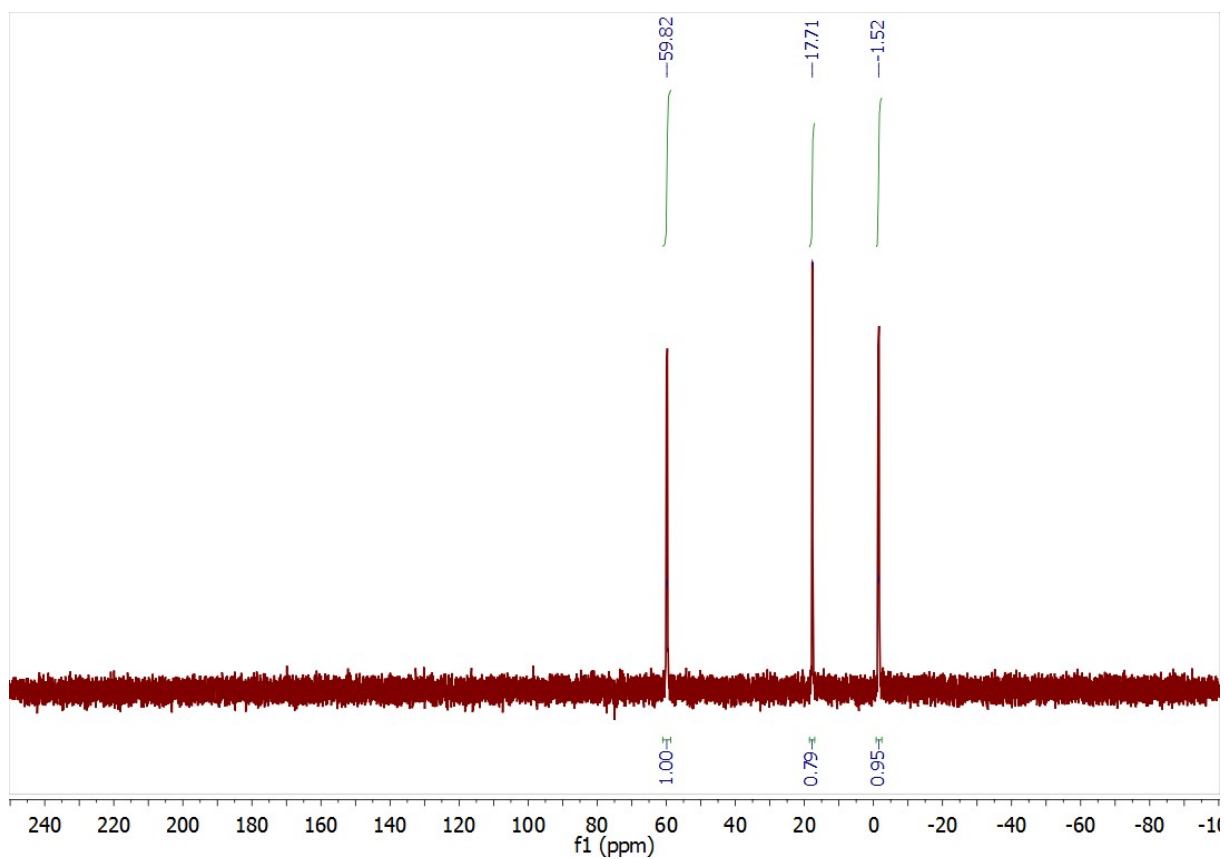
Figure SI-47 ^{31}P NMR spectrum of [(**L2**)Pd(O$_3$SCF$_3$)](O$_3$SCF$_3$) in CD$_2$Cl$_2$ at rt and ap.
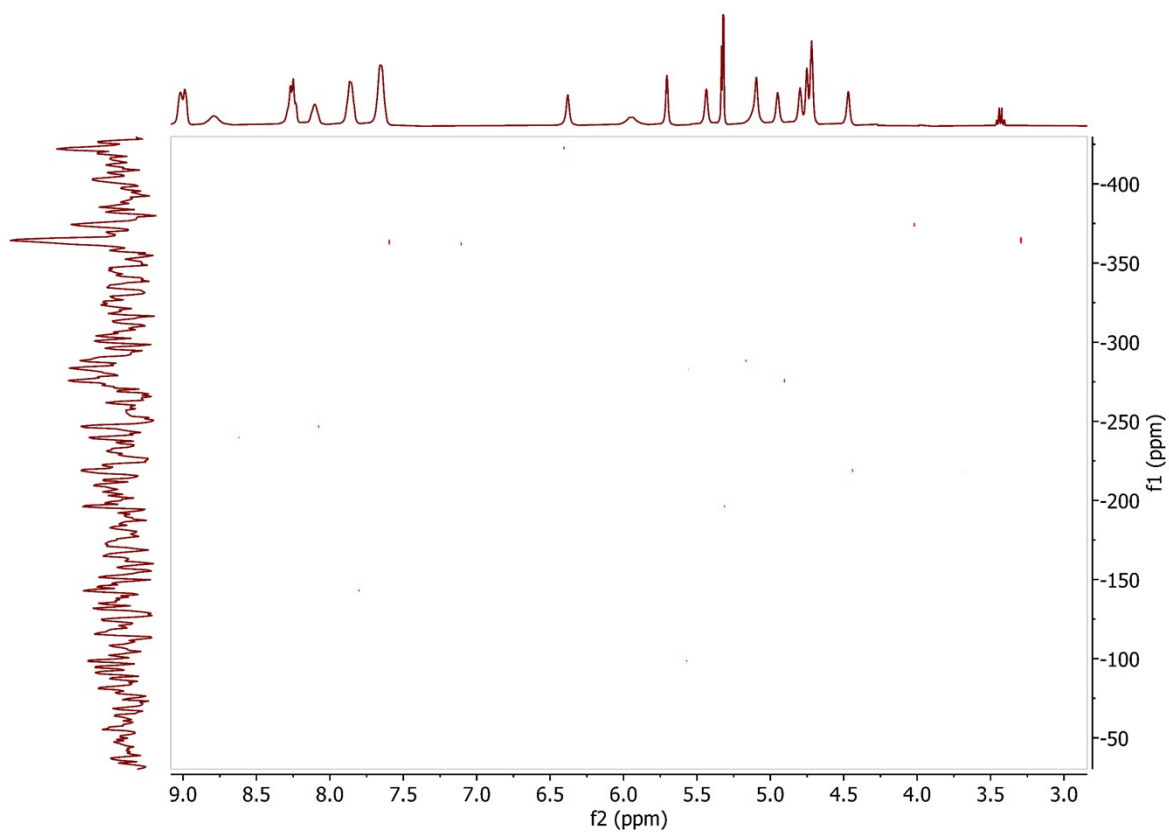
Figure SI-48 $^{1}H/^{15}N$-HMBC NMR spectrum (400 MHz) of [(**L2**)Pd(O$_3$SCF$_3$)](O$_3$SCF$_3$) in CD$_2$Cl$_2$ at rt. Transfer delay 100 ms (J = 5 Hz). No signals assignable to a Py-N are visible.
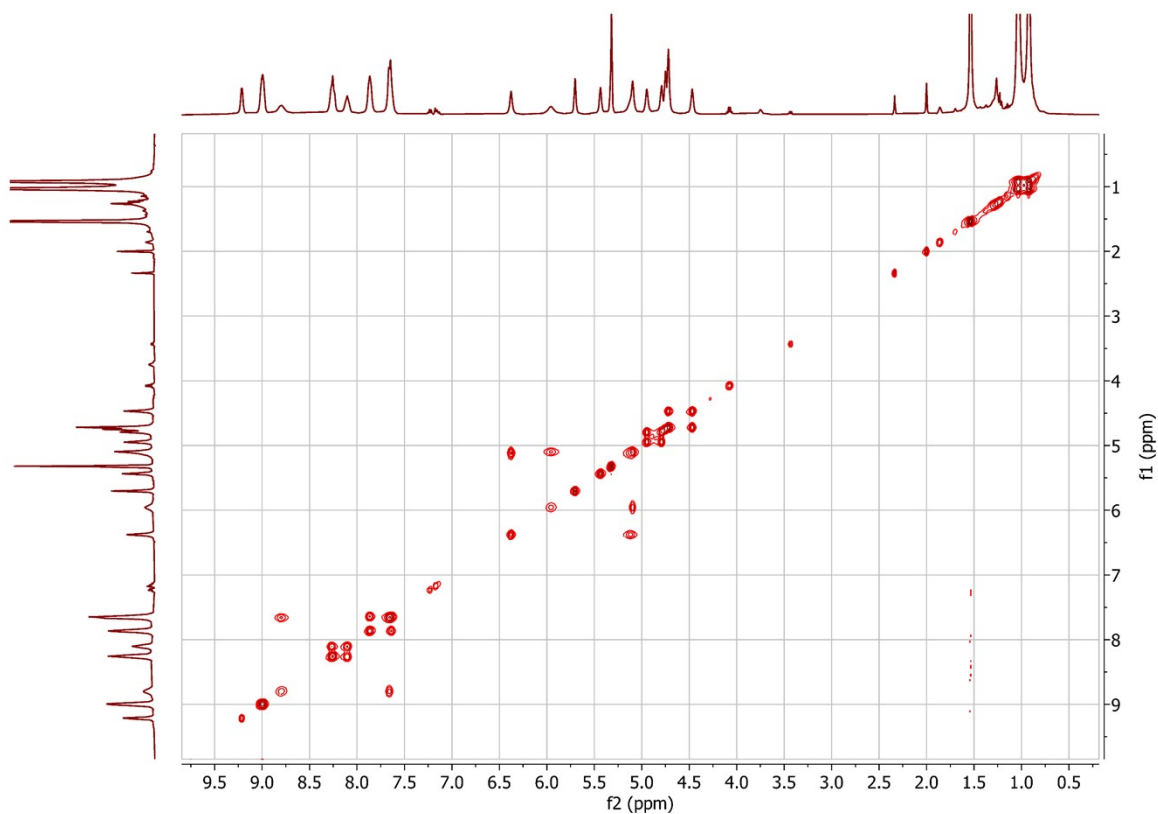
Figure SI-49 ^{1}H-^{1}H EXSY NMR spectrum (400 MHz) of [(**L2**)Pd(O$_3$SCF$_3$)](O$_3$SCF$_3$) in CD$_2$Cl$_2$ at rt. Short spin evolution times (0.5 s) were picked to show spin correlations due to chemical exchange rather than spatial correlations. The top trace (1D spectrum) is phosphorus-decoupled.
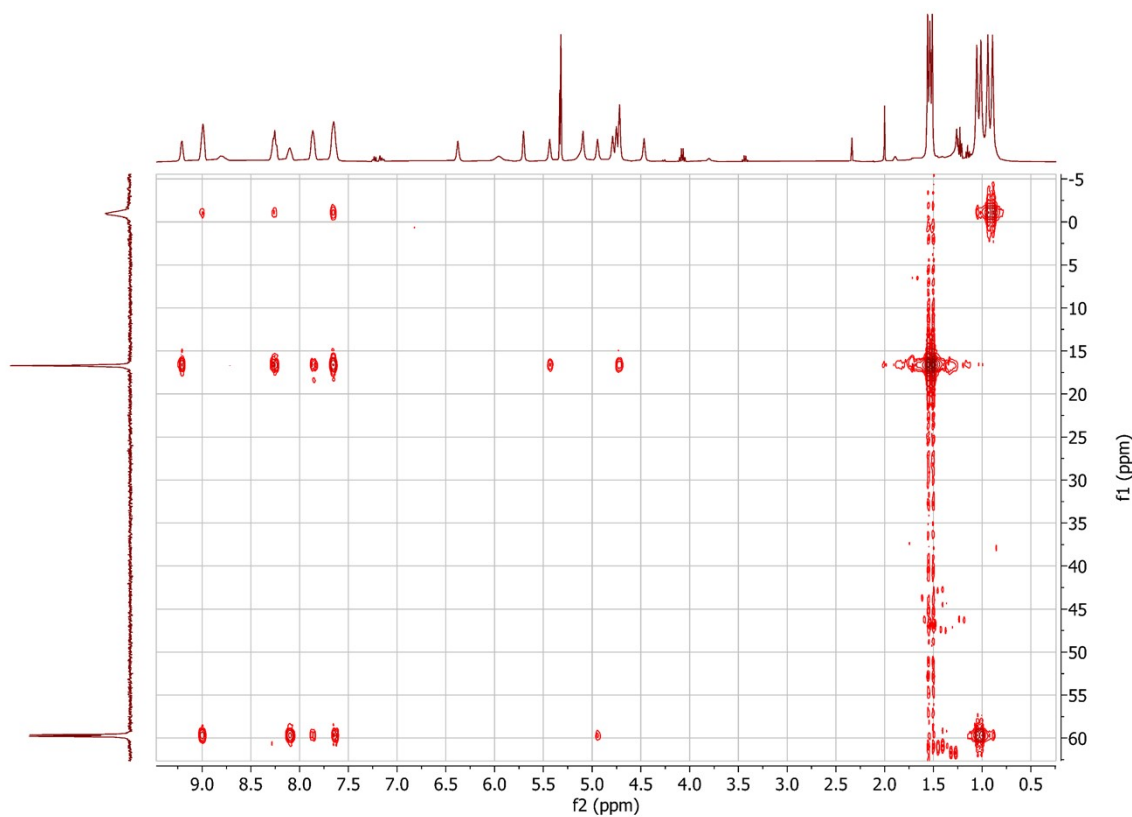
Figure SI-50 ^{1}H/^{31}P-HMBC NMR spectrum (400 MHz) of [(**L2**)Pd(O$_3$SCF$_3$)](O$_3$SCF$_3$) in CD$_2$Cl$_2$ at rt. Transfer delay 62.5 ms. The top trace (1D spectrum) is phosphorus-coupled.

—77.98
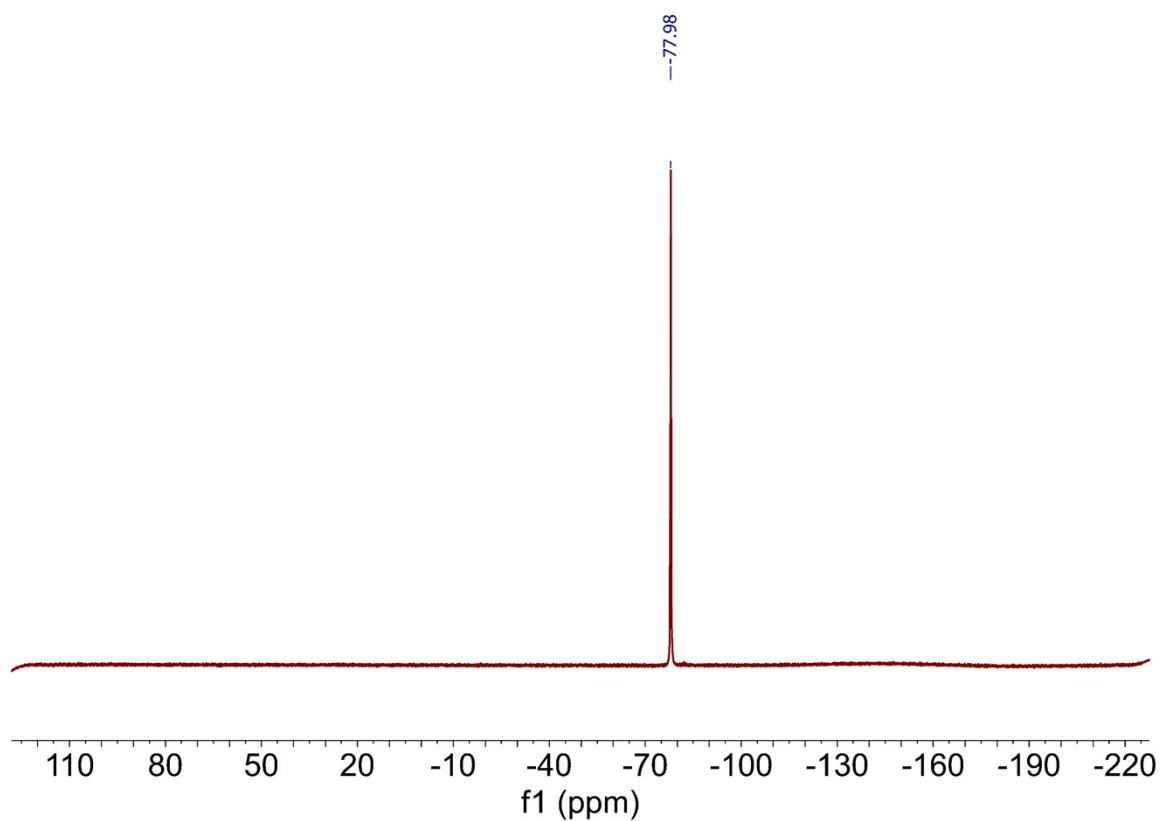
Figure SI-51 ^{19}F NMR spectrum (376 MHz) of [(**L2**)Pd(O$_3$SCF$_3$)](O$_3$SCF$_3$) in CD$_2$Cl$_2$ at rt.

Pd/**L2**$_{mix}$ with **L2**$_{mix}$ → **L2**-*rac*:**L2**-*meso* = 50:50

2B$_{maj}$-*rac*-**L2** (50%)

2B$_{min}$-*meso*-**L2**/1 (5%)

2B$_{min}$-*meso*-**L2**/3 (5%)

2B$_{min}$-*meso*-**L2**/2 (40%)
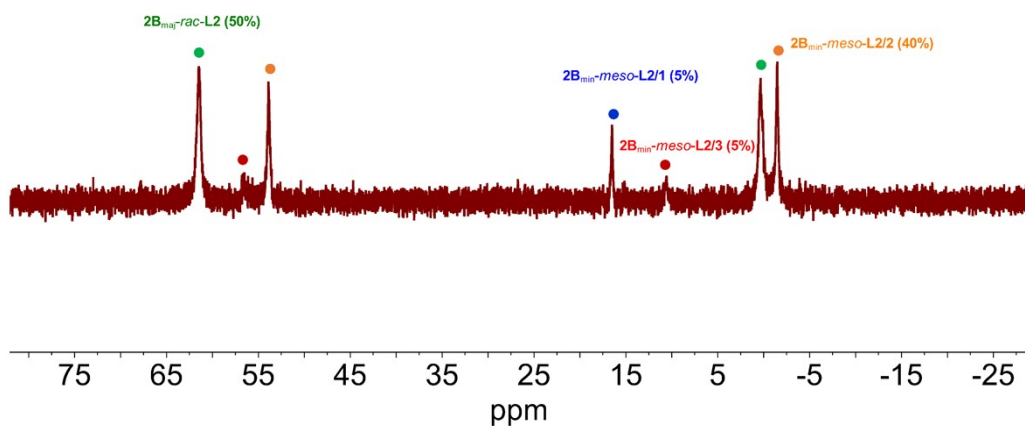
Figure SI-52 ^{31}P NMR spectrum of mixture consisting of **2B$_{maj}$** (**2B**-*rac*-**L2**), **2B$_{min}$** (**2B**-*meso*-**L2**/1), **2B**-*meso*-**L2**/2, **2B**-*meso*-**L2**/3 in CD$_2$Cl$_2$ at rt.

SI-I: Acid-free synthetic pathway of [(P∩P)Pd(O$_3$SCF$_3$)](O$_3$SCF$_3$) (P∩P = **L1**, **L2**)

General experimental procedures

a) Synthesis of [(P∩P)PdCl$_2$]
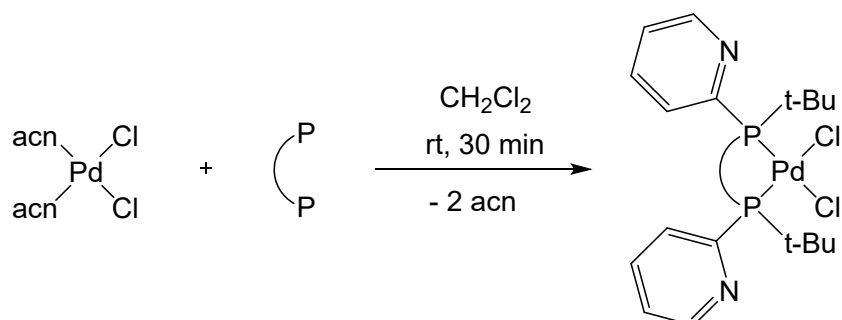
[Pd(acn)$_2$(Cl)$_2$] (51.8 mg, 0.2 mmol) and the ligand (0.2 mmol) (**L: L1, L2**) were weighed into a Schlenk flask and dissolved in 5 mL of dry THF under argon. The resulting solution was stirred for 30 min and then evaporated until 1 mL was left. Then 5 mL of dry diethylether were added, precipitating a yellow solid. The solid was filtered off and washed with dry diethylether. Drying *in vacuo* resulted in a yellow powder comprised of the complex [(**L**)PdCl$_2$]. Crystals suitable for X-ray crystallography could be produced by dissolution in dry methanol, addition of a small amount of heptane and slow evaporation over multiple days in the refrigerator.

[(**L1**)PdCl$_2$]

yellowish solid, 79 % yield.

¹H NMR (300 MHz, dichloromethane-d_2) δ 8.66 (dm, J = 4.8 Hz, 2H), 8.39 (br. s, 2H), 7.70 (m, 2H), 7.35 (m, 2H), 6.97 (m, 2H), 6.71 (br. s, 2H), 3.72 (br. s, 4H), 1.37 (d, J = 16.6 Hz, 18H).
³¹P NMR (122 MHz, dichloromethane-d_2) δ 31.7 ppm (br. s). The purity of the product is 96 % according to the ³¹P NMR spectrum.
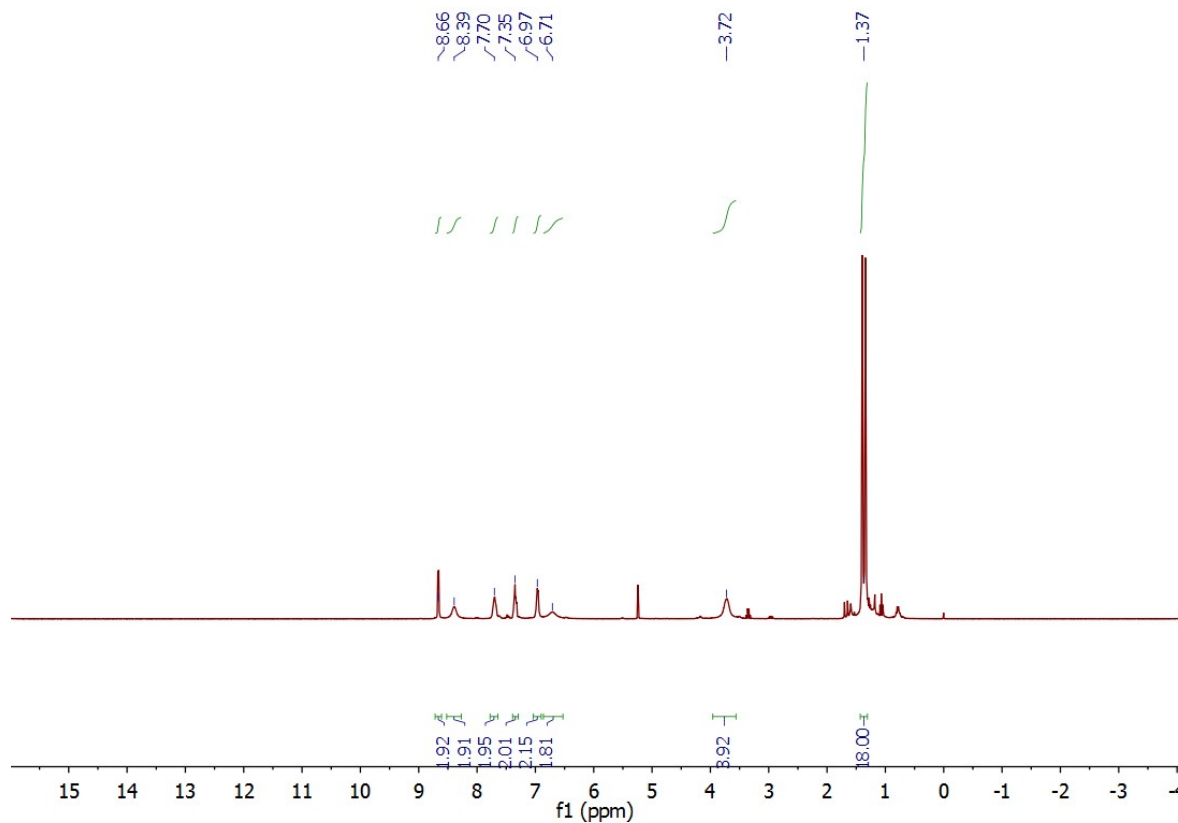
Figure SI-53 ^{1}H NMR spectrum of [(**L1**)PdCl$_2$] in CD$_2$Cl$_2$ at rt and ap.
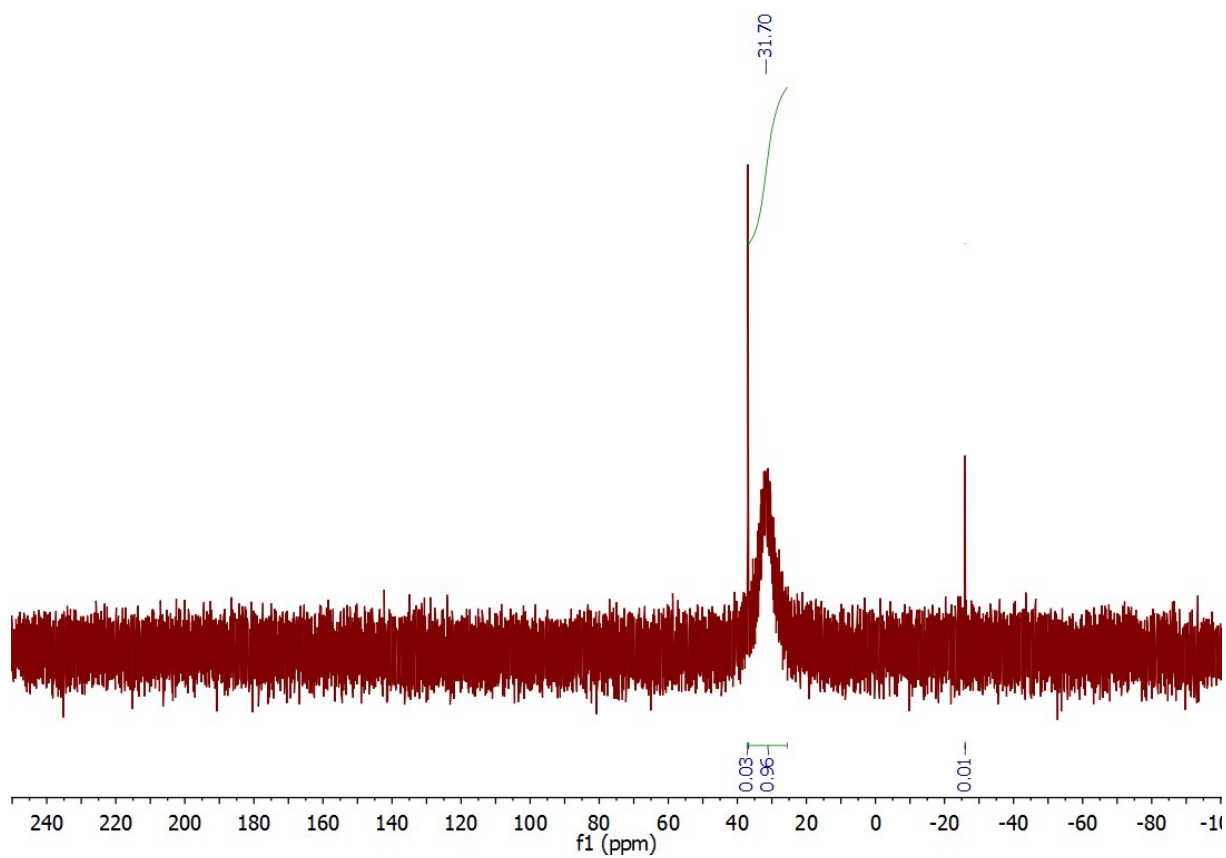
Figure SI-54 ^{31}P NMR spectrum of [(**L1**)PdCl$_2$] in CD$_2$Cl$_2$ at rt and ap.

SI-57

[(**L2**)PdCl$_2$]

yellow solid, 76 % yield

¹H NMR (300 MHz, dichloromethane-d_2) δ 8.80 (br. ps. t, J = 7.0 Hz, 2H, Py-H), 8.71 (d, J = 4.5 Hz, 2H Py-H), 7.83 (m, 2H, Py-H), 7.39 (m, 2H, Py-H), 4.45 (br. s, 2H, Cp-H), 4.28 (br. s, 2H, Cp-H), 4.15 (br. s, 2H, Cp-H), 3.98 (br. s, 2H, Cp-H), 1.24 (d, J = 16.3 Hz, 18H, tBu-H).
³¹P NMR (122 MHz, dichloromethane-d_2) δ 45.92 (br. s).
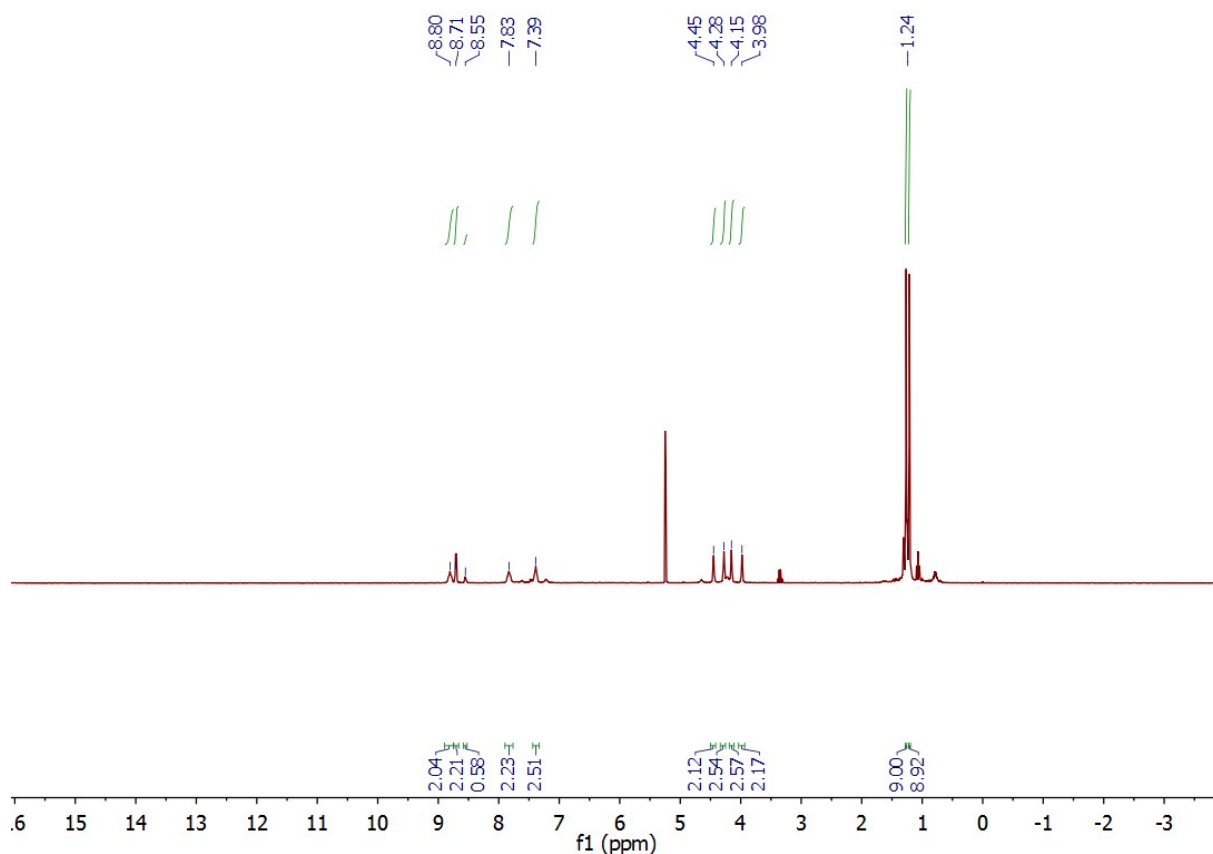
Figure SI-55   ¹H NMR spectrum of [(**L2**)PdCl$_2$] in CD$_2$Cl$_2$ at rt and ap.

—45.92
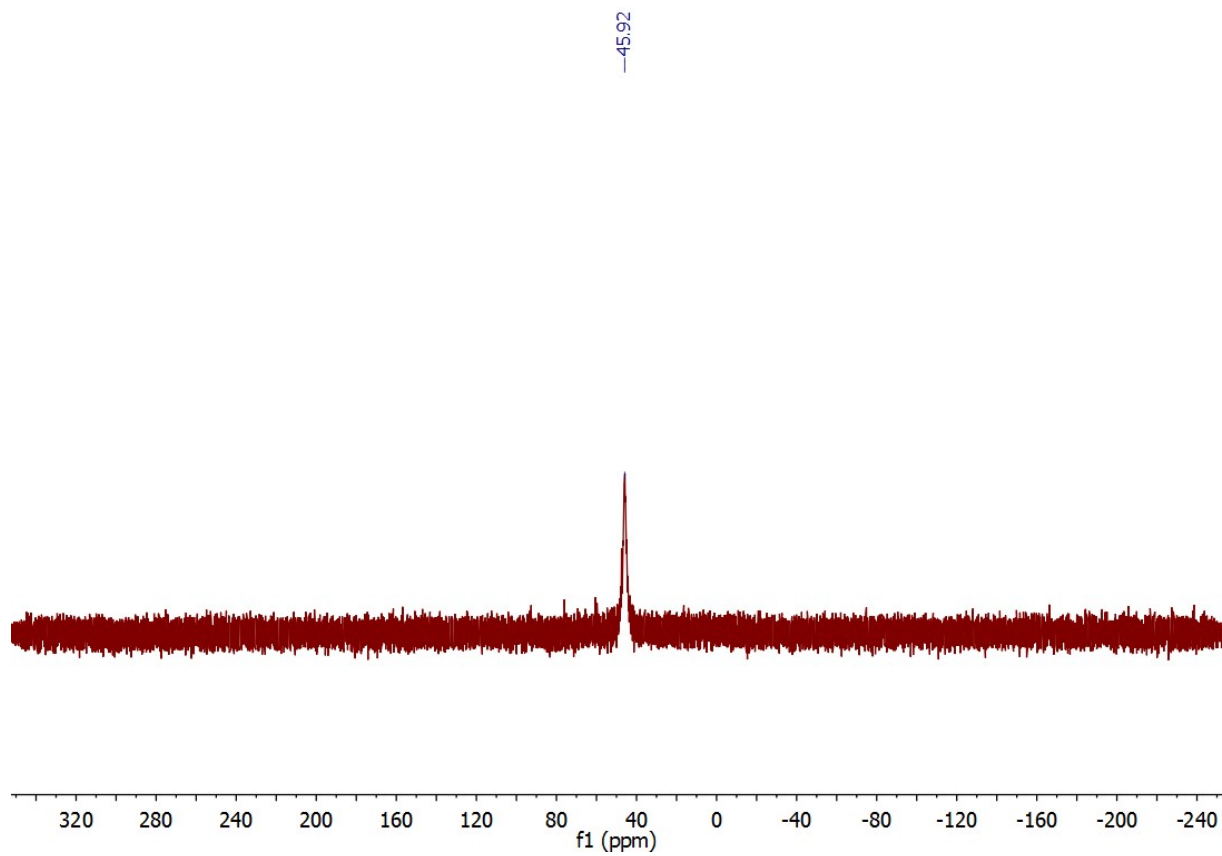
Figure SI-56 ^{31}P NMR of [(**L2**)PdCl$_2$] in CD$_2$Cl$_2$ at rt and ap.

b)   Synthesis of [(P∩P)Pd(O₃SCF₃)](O₃SCF₃) starting from [(P∩P)PdCl₂]
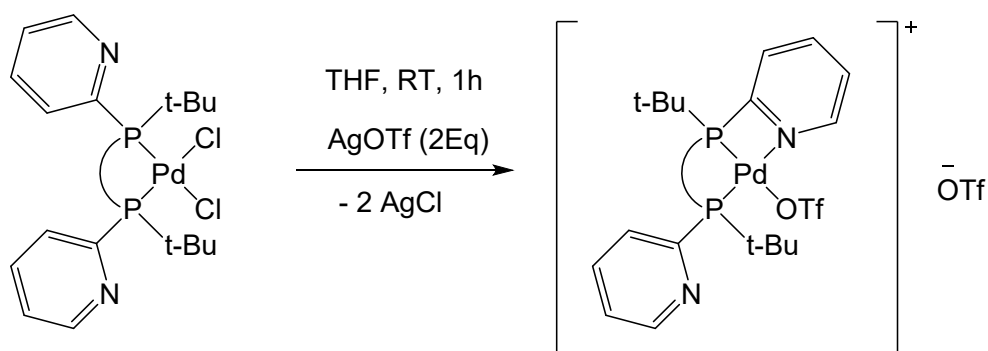
[(P∩P)PdCl₂] (0.04786 mmol) was weighed into a Schlenk flask and dissolved in 2.5 mL of dry THF under argon. Another solution was prepared by dissolving 2 Eq. of AgOTf (77.7 mg, 0.09572 mmol) in dry THF. The AgOTf solution was added dropwise while stirring at rt. The yellow solution almost immediately changed its colour while precipitation of AgCl occurred (dark red for py^{t}bpf, pale yellow for py^{t}bpx). Stirring commenced for 1 h at room temperature. After that, the AgCl was filtered off and washed with dry THF. The filtrate was reduced in vacuo to 1 mL and diluted with 5 mL of dry heptane to precipitate the product. The resulting suspension was stirred for 1 h. The solid was filtered off, washed with dry heptane and dried in vacuo overnight.

[(**L1**)Pd(O₃SCF₃)](O₃SCF₃)

yellowish powder, 62.1 % yield

³¹P NMR (122 MHz, dichloromethane-d_2) δ 33.71 (d, ^{2}J(P,P) = 15.1 Hz), -4.73 (d, ^{2}J(P,P) = 15.1 Hz).
Further signal: δ 3.31 (s) (impurity)
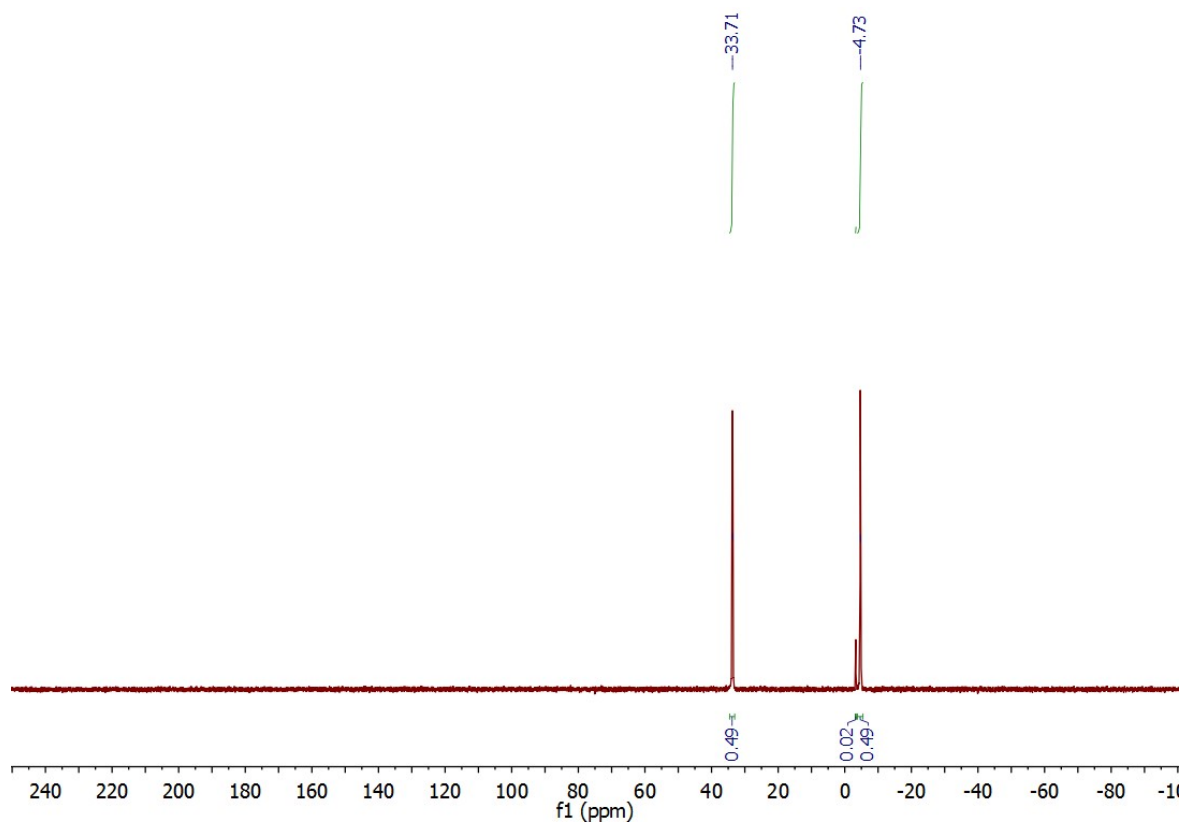
Figure SI-57 ^{31}P NMR spectrum of [(**L1**)Pd(O$_3$SCF$_3$)](O$_3$SCF$_3$) synthesized without acid in CD$_2$Cl$_2$ at rt and ap. Only small amounts of impurities present (~2.0 %).

[(**L2**)Pd(O$_3$SCF$_3$)](O$_3$SCF$_3$)

red powder, 88.2 % yield

^{31}P NMR (122 MHz, dichloromethane-d_2)
Major: δ 60.97 (d, ^{2}J(P,P) = 29.6 Hz), 0.07 (d, ^{2}J(P,P) = 29.6 Hz).
Minor: δ 16.58 (s)
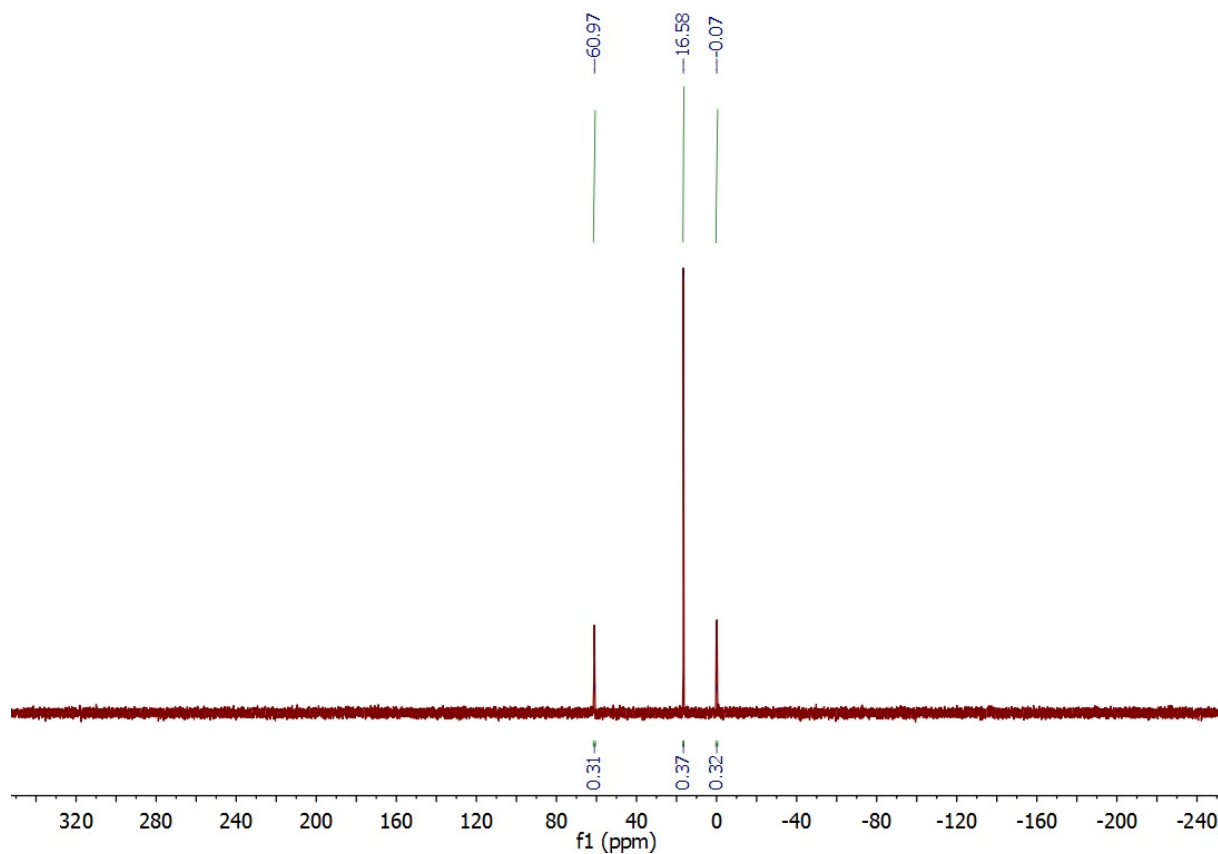
Figure SI-58 ^{31}P NMR of [(**L2**)Pd(O$_3$SCF$_3$)](O$_3$SCF$_3$) synthesized without acid in CD$_2$Cl$_2$ at rt and ap.

SI-J: X-ray crystal structure analysis of [(**L1**)Pd^{II}(O$_3$SCF$_3$)](O$_3$SCF$_3$) (a) and [(**L1**)Pd^{II}Cl]Cl (b)

Data were collected on a Bruker Kappa APEX II Duo diffractometer. The structures were solved by direct methods (SHELXS-97: Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112.) and refined by full-matrix least-squares procedures on F^2 (SHELXL-2014: Sheldrick, G. M. *Acta Cryst.* **2015**, *C71*, 3.). XP (Bruker AXS) was used for graphical representations. CCDC 1935038, 1935039 and 2059622 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Crystal data of **a**: C$_{28}$H$_{34}$F$_6$N$_2$O$_6$P$_2$PdS$_2$, M = 841.03, triclinic, space group $P\bar{1}$, a = 11.2734(7), b = 12.1729(7), c = 13.5903(8) Å, α = 73.9005(13), β = 72.8892(13), γ = 73.6404(12)°, V = 1671.40(17) Å^3, T = 150(2) K, Z = 2, 55544 reflections measured, 8068 independent reflections (R_{int} = 0.0198), final R values ($I > 2\sigma(I)$): R_1 = 0.0201, wR_2 = 0.0501, final R values (all data): R_1 = 0.0207, wR_2 = 0.0506, 430 parameters.

Crystal data of **b**: C$_{29.4}$H$_{40.8}$Cl$_{8.8}$N$_2$P$_2$Pd, M = 902.54, monoclinic, space group $P2_1/n$, a = 15.2620(6), b = 12.8154(5), c = 20.9917(8) Å, β = 108.5348(16)°, V = 3892.8(3) Å^3, T = 150(2) K, Z = 4, 50050 reflections measured, 9395 independent reflections (R_{int} = 0.0269), final R values ($I > 2\sigma(I)$): R_1 = 0.0317, wR_2 = 0.0781, final R values (all data): R_1 = 0.0395, wR_2 = 0.0837, 426 parameters.
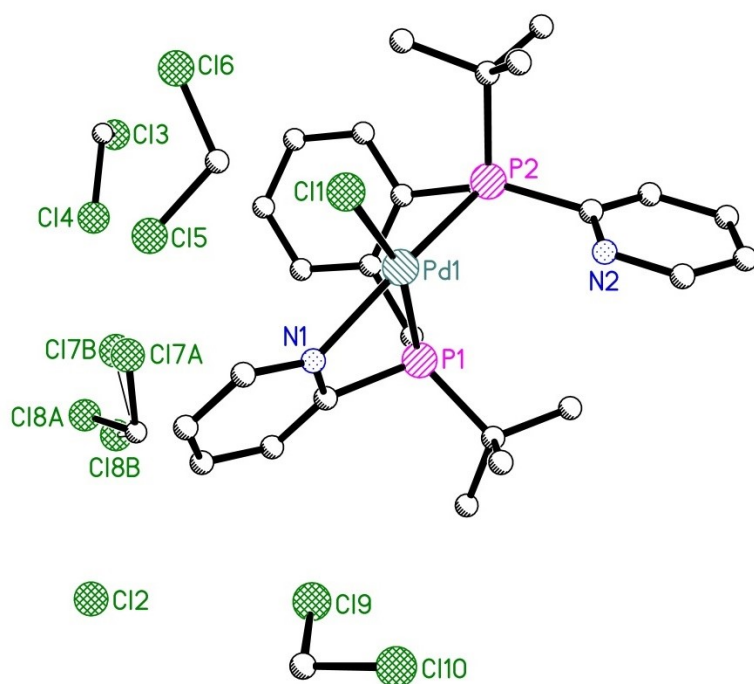
Figure SI-59   Ball and stick representation of [(**L1**)Pd^{II}Cl]Cl **(b)**. Hydrogen atoms are omitted for clarity.

Crystal data of (**L1**-*meso*)·BH$_3$: C$_{26}$H$_{40}$B$_2$N$_2$P$_2$, M = 464.16, triclinic, space group P $\bar{1}$, a = 9.1591(8), b = 11.3142(10), c = 15.1394(14) Å, α = 103.273(2), β = 102.525(2), γ = 105.201(2)°, V = 1407.9(2) Å^3, T = 150(2) K, Z = 2, 61035 reflections measured, 6782 independent reflections (R_{int} = 0.0246), final R values ($I > 2\sigma(I)$): R_1 = 0.0328, wR_2 = 0.0882, final R values (all data): R_1 = 0.0361, wR_2 = 0.0919, 319 parameters.
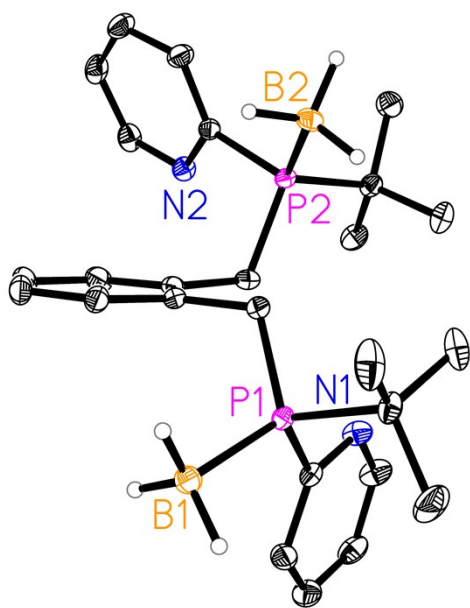
Figure SI-60   Molecular structure of (L1-*meso*)·BH$_3$ Displacement ellipsoids correspond to 30% probability. C-bound hydrogen atoms are omitted for clarity.

SI-K: *In situ* formation of Pd catalyst complexes

General experimental procedure

A 10 mL Schlenk flask was charged with Pd-precursor (30.0 µmol with respect to mononuclear Pd) (Pd(OAc)$_2$, Pd(acac)$_2$, Pd(dba)$_2$, Pd$_2$(dba)$_3$, PdCl$_2$), diphosphine (60.0 µmol) (L1, L2) and benzoquinone (16.2 mg, 150.0 µmol) and the contents dissolved in 1 mL of dry dichloromethane-d_2 under argon. The solution was stirred for a few minutes. Then, trifluoromethanesulfonic acid (22.5 mg, 13.3 µL, 150 µmol) was added via a 100 µL syringe. The solution was mixed and then transferred into a J. Young NMR-tube for NMR spectroscopic experiments.

SI-L: Methoxycarbonylation of industrial relevant alkenes catalyzed by Pd/L (L = L1, L2)

The methoxycarbonylation of ethylene with various Pd-precursors using diphosphine ligands L1 or L2
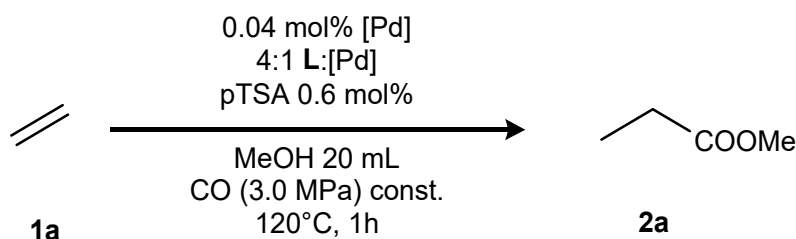
0.04 mol% [Pd]
4:1 **L**:[Pd]
pTSA 0.6 mol%

MeOH 20 mL
CO (3.0 MPa) const.
120°C, 1h

1a

2a

General experimental procedure

100 mL steel autoclave was charged with Pd-precursor ((**L**)Pd(dba), Pd(acac)$_2$, Pd$_2$(dba)$_3$) (0.04 mol% Pd), diphosphine ligand (0.12 mol% for (**L**)Pd(dba), else 0.16 mol%) and *p*-toluenesulfonic acid (pTSA) (61.1 mg, 0.6 mol%) under argon atmosphere. With a mL-syringe 20 mL methanol was introduced into the autoclave. Then ethylene (1.5 g, 53.6 mmol) was added (mass control by balance). CO (3.0 MPa) was introduced into the autoclave at 23 °C and the reaction was carried out until no pressure drop was detected, but no longer than 20 h. Pressure inside the autoclave was measured constantly. The reaction was stopped by cooling the autoclave to room temperature. Remaining gas was released slowly. 3.0 mL isooctane was added into the reaction mixture as the internal standard and the yield was measured by GC analysis.

The methoxycarbonylation of diisobutylene with various Pd-precursors using diphosphine ligands L1 or L2
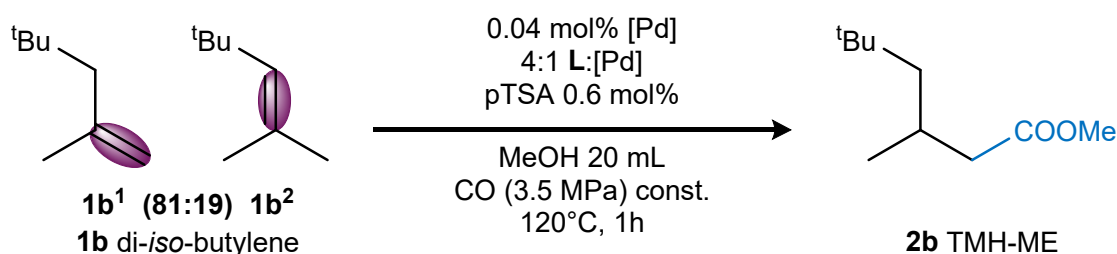
^{t}Bu ^{t}Bu

0.04 mol% [Pd]
4:1 **L**:[Pd]
pTSA 0.6 mol%

MeOH 20 mL
CO (3.5 MPa) const.
120°C, 1h

^{t}Bu   COOMe

1b^1 (81:19) 1b^2
1b di-*iso*-butylene

2b TMH-ME

General experimental procedure

100 mL steel autoclave was charged with Pd-precursor ((**L**)Pd(dba), Pd(acac)$_2$, Pd$_2$(dba)$_3$) (0.04 mol% Pd), diphosphine ligand (0.12 mol% for (**L**)Pd(dba), else 0.16 mol%) and p-toluenesulfonic acid (pTSA) (45.7 mg, 0.6 mol%) under argon

atmosphere. With a mL-syringe 20 mL methanol was introduced into the autoclave. The autoclave was purged three times with CO (10 bar) and finally charged with CO (1.0 MPa) and heated to 120°C. After 10 minutes at constant reaction temperature the substrate diisobutene (4.49 g, 40 mmol) applied with additional CO pressure was charged into the autoclave. Pressure was adjusted to 3.5 MPa and kept constant during the reaction. It was carried out until no pressure drop was detected, but no longer than 20 h. Pressure inside a CO-buffer tank was monitored on-line automatically. The reaction was stopped by cooling the autoclave to room temperature. Remaining gas was released slowly. 3.0 mL isooctane was added into the reaction mixture as the internal standard and the yield was measured by GC analysis.

SI-M: Catalytic activity of diastereomerically pure Pd complexes of the type [**L2**Pd(C$_5$H$_5$NO$_2$)]

To compare the activity of the diastereomeric palladium complexes **[(L2-*rac*)Pd(C$_5$H$_5$NO$_2$)]** and **[(L2-*meso*)Pd(C$_5$H$_5$NO$_2$)]** in the methoxy-carbonylation of 1-octene, following experiments were carried out:
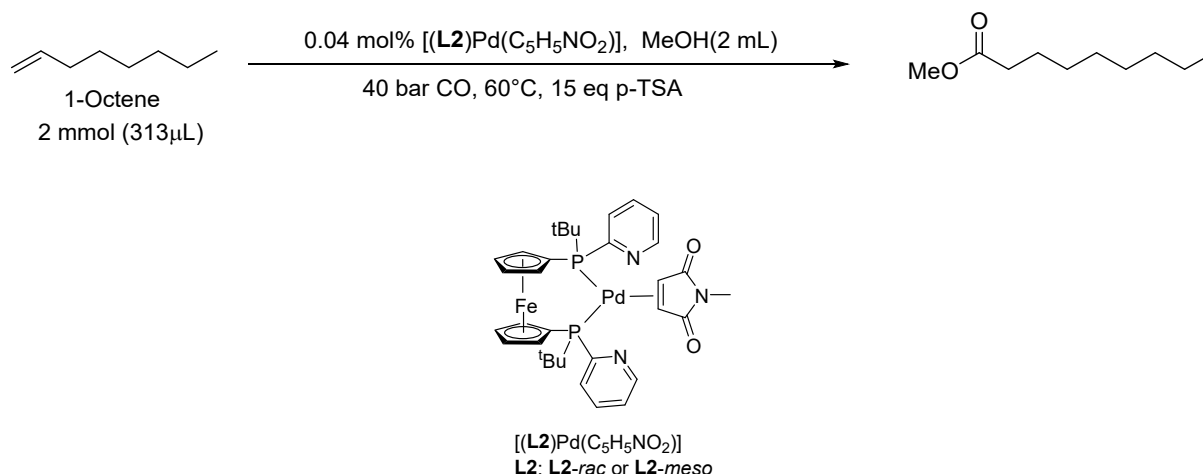
2.93 mg (0.004 mmol) each of the complexes are weighted in a Schlenk tube and was dissolved in 5 mL MeOH. In a third Schlenk tube 22,8 mg (0.12 mmol) (p-TSA·H$_2$O was solved in 10 mL MeOH. In two 12 mL vials with septum equipped with needle and stirring bar each of 1mL stock solution of the complexes and 1 ml of the p-TSA stock solution and 310 µL (2mmol) 1-octene were added. The two vials are in an aluminum-plate, which was put in a 300 mL Parr autoclave. The autoclave was pressurized with 40 bar CO and heated in a preheated 60°C aluminum block. After 15 minutes reaction time the autoclave was cooled with ice and the CO was carefully released. In each vial 300µL iso-octane as internal standard was added. Next, 150 µL of the reaction solution diluted in 1.5 mL ethyl acetate was submitted to the GC to determine the yield. In the same manner a reaction with 30 minutes reaction time was carried out.

SI-N: In situ spectroscopic investigations on catalytically relevant species

HP-NMR spectroscopic measurements for detection of possible alkyl complexes
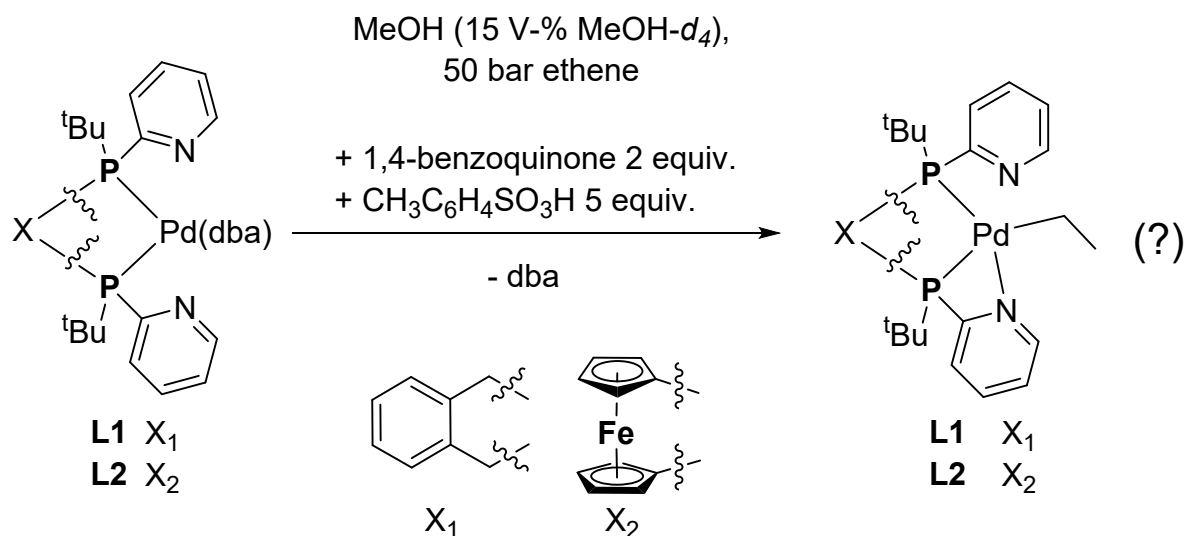
The catalyst solution was prepared under inert atmosphere in a Schlenk flask by dissolving [(P∩P)Pd(dba)]-complex (0.09 mmol, 69.9 mg (**L1**), 77.1 mg (**L2**)) in 3 mL of dry methanol, adding pTSA (77.4 mg, 0.45 mmol) and stirring for a few minutes. A sample of the solution was collected and analyzed to check if the resting state was formed. After this, the solution was transferred into a sapphire NMR tube, pressurized with 50 bar of ethylene and thoroughly shaken. The samples have been analyzed via NMR spectroscopy to monitor possible changes of the reaction mixture in comparison to a "control"-sample kept under 0.1 MPa of argon.

HP NMR-spectroscopic experiments were conducted using a NMR-cell setup from Deadalus (Aston, USA) with a 5 mm OD (3.4 mm ID) sapphire tube and a cell made of titanium. https://daedalusinnovations.com/high-pressure-nmr/

NMR measurements at 0.1 MPa have been conducted using a normal thin wall J. Young tube.

Pd/L1

Two similar solutions were analyzed by NMR spectroscopy with and without the addition of ethene. For the sample under 0.1 MPa of argon at T = 297 K the same NMR spectroscopic features for a complex of the type [(**L**)Pd(O$_3$SR)](O$_3$SR) were

observed. Addition of 5.0 MPa of ethene did not lead to any significant changes in the ^{1}H and ^{31}P NMR spectra.

Table SI-2   Selected ^{31}P{^{1}H}-NMR properties of the Pd/**L1** catalyst system related to HP NMR spectroscopic measurements. [Pd] = 30 mM, [pTSA]/[Pd] = 10, [BQ]/[Pd] = 10, solvent: MeOH, T = 297 K.

Gas atmosphere	Pd/**L1** $\delta(^{31}$P)/ppm
0.1 MPa Ar	33.9 (s), -6.9 (s)
5.0 MPa C$_2$H$_4$	33.6 (s), -7.1 (s)

Attempts to detect a Pd-alkyl species (Pd-CH$_2$ group) by ^{1}H-^{13}C 2D correlation techniques failed. A spin-saturation transfer experiment[8] (irradiation at the frequency of free ethylene at 5.36 ppm for 4 s) did not help to detect C$_2$H$_4$ incorporation in a transition metal species (as it was possible for metallacyclic compounds)[9].

Pd/L2

The sample under 0.1 MPa of argon at T = 297 K showed the same NMR spectroscopic features, expected for the mixture of the major unsymmetric complex of the type [(**L**)Pd(O$_3$SR)](O$_3$SR) and the minor symmetric isomer (see discussion in the manuscript).

Because of strong line broadening for the unsymmetric complex species, represented by the ^{31}P signals at ca. 60 and − 2 ppm at ambient temperature, spectra were also recorded at 263 K. Only minor changes occured at ethylene addition (5.0 MPa), slight changes in the chemical shifts ^{1}H, ^{31}P for instance. Attempts to detect a Pd-alkyl species (Pd-CH$_2$ group) by ^{1}H NOE resp. exchange spectroscopy (1D selective and 2D correlation techniques) were unsuccessful.

Table SI-3   Selected ^{31}P{^{1}H}-NMR properties of the Pd/**L2** catalyst system related to HP NMR spectroscopic measurements. [Pd] = 30 mM, [pTSA]/[Pd] = 10, [BQ]/[Pd] = 10, solvent: MeOH, T = 263 K.

Gas atmosphere	Pd/**L2** major $\delta(^{31}$P)/ppm	Pd/**L2** minor $\delta(^{31}$P)/ppm
0.1 MPa Ar	59.6 (s), -1.6 (s)	21.7 (s)
5.0 MPa C$_2$H$_4$	59.3 (s), -1.8 (s)	24.0 (s)
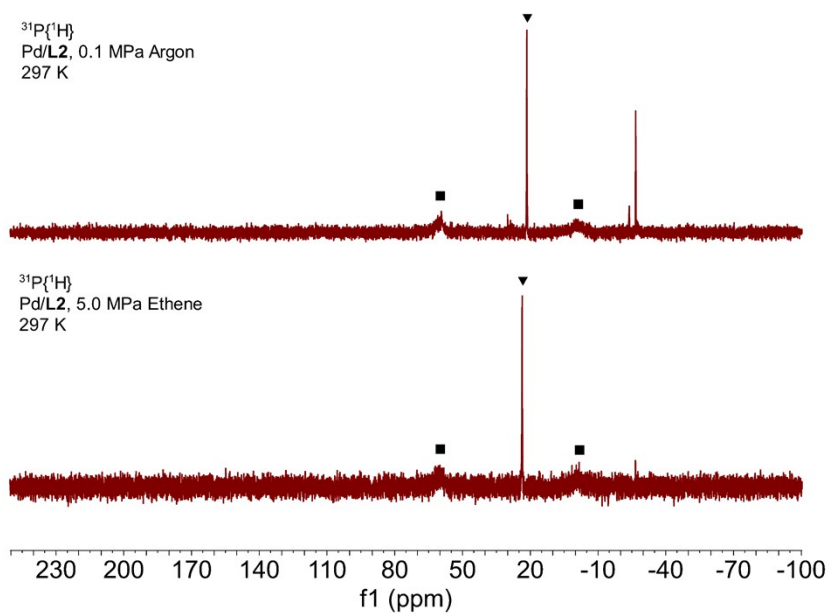
Figure SI-61 $^{31}P\{^1H\}$ NMR spectra for Pd/**L2** at 0.1 MPa of argon and 5.0 of ethene (297 K). ■ Major unsymmeric isomer, ▼ minor symmetric isomer. Other signals represent unknown impurities.
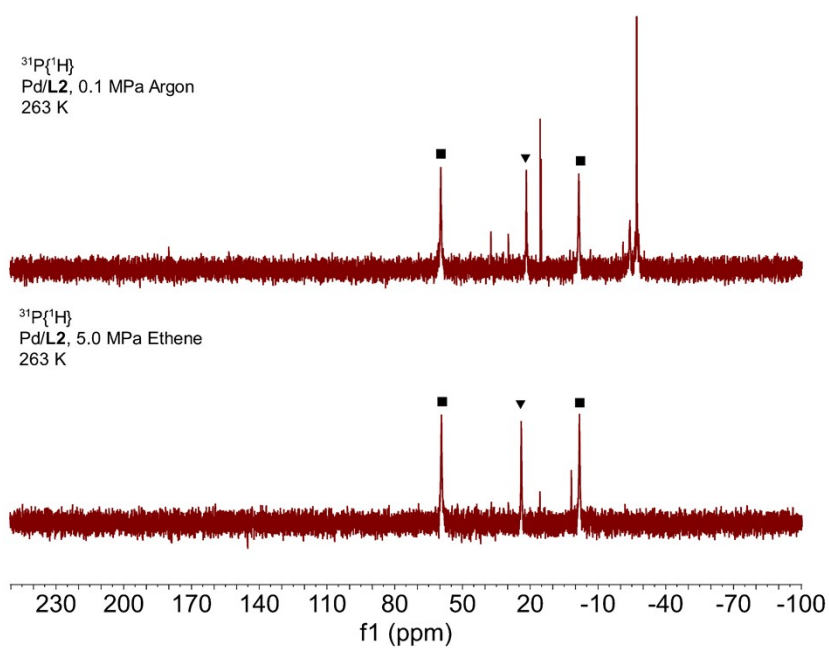
Figure SI-62 $^{31}P\{^1H\}$ NMR spectra for Pd/**L2** at 0.1 MPa of argon and 5.0 of ethene (263). ■ Major unsymmeric isomer, ▼ minor symmetric isomer. Other signals represent unknown impurities.

HP-FTIR spectroscopic measurements for detection of possible acyl complexes

General remarks

Prior to the *in situ* FTIR experiments, background spectra of the solvent or the catalyst solution have been recorded at respective experimental conditions (before and/or after addition of gases).

Reactions for *in situ* infrared spectroscopic analysis were performed in a HP-FTIR apparatus consisting of a 25 ml stainless steel cylinder (miniature cylinder, Swagelok) with a magnetic stirrer bar connected to a pressurizable and heatable transmission flow-through IR cell. Pressurization facilities were installed for ethene as well as carbon monoxide.

Transport of the liquid reaction solution through the IR cell and back to the reaction vessel was performed by a micro gear pump (mzr-7255, HNP Mikrosysteme GmbH, Parchim, Germany). The micro gear pump was set to 600 rpm (displacement volume = 48 µL).

For the infrared spectroscopic measurements, a Bruker Tensor 27 FTIR spectrometer with a MCT-A detector was used. CaF_2 (Korth Kristalle GmbH, Kiel, Germany) was used as window material. The optical path length was 0.1 mm. FTIR spectra have been recorded between 3950 and 900 cm^{-1} with a spectral resolution of 2 cm^{-1}. Ten (or less) scans were collected per FTIR spectrum (double-sided, forward–backward).

All preparations of solutions and transfers were carried out under argon atmosphere by using standard Schlenk techniques.

FTIR-spectroscopic monitoring during methoxycarbonylation of ethene using [Pd(acac)$_2$]/L1

A solution (10 ml) of [Pd(acac)$_2$], **L1** and *p*-toluoenesulfonic acid in methanol was prepared ([Pd] = 5 mM, [**L1**]/[Pd] =4, [PTSA]/[Pd] = 15) at room temperature under argon. The clear liquid mixture was transferred into the HP-IR apparatus. The temperature was set to 30 °C and 0.5 MPa of ethene was introduced into the system. In the next step 0.5 MPa of carbon monoxide was added. Simultaneously the collection of infrared spectra was started to monitor the reaction.

Remark: The in situ system [Pd(acac)$_2$]/**L1** was considered as suitable since the formation of a respective sulfonate complexes [**L1**Pd(O$_3$SR)](O$_3$SR) was observed by NMR spectroscopy.

FTIR-spectroscopic monitoring during alkoxycarbonylation of ethene using [LPd(dba)]

Remark: We decided to perform these investigations in *tert*-amylalcohol with the intention that this bulky alcohol could slow down the alcoholysis and thus establish best possible conditions for the population of a respective acyl complex (propionyl complex). We have chosen [(**L**)Pd(dba)] as a precursor because the formation of respective sulfonate complexes was found to be optimal. The overall Pd concentration was adjusted to 30 mM in order to considerably raise the change to detect possible acyl complexes.
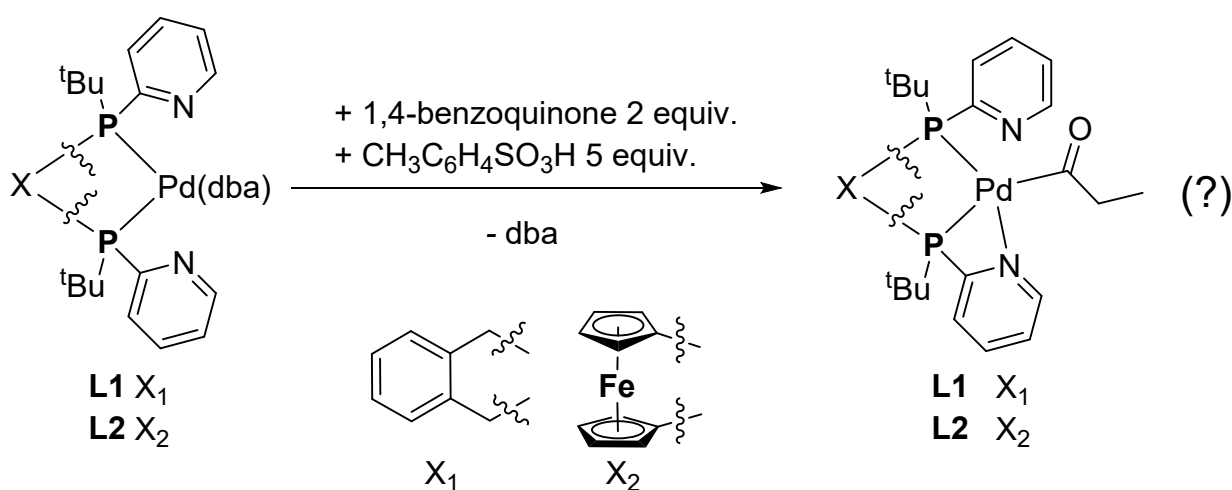
[(L∩L)Pd(dba)] (0.15 mmol) was weighed into a 25 mL Schlenk flask and dissolved in 2.5 mL of the desired solvent. 2.5 mL of a second solution were prepared by dissolving dry pTSA (15.6 mg, 0.75 mmol) in 2.5 mL of the same solvent used for the other solution. Then, the pTSA solution was transferred into the stirred complex solution. The mixture was left stirring for a few minutes and was then injected into a 25 mL stainless steel autoclave connected to the FT/IR spectrometer fitted with a flow cell. The mixture was set to θ = 30 °C followed by the addition of 10 bar of ethylene. After 30 min of stirring, 10 bar of CO were added and the mixture was stirred for another hour. FT/IR spectra were recorded over the course of the whole experiment.

HP-FTIR spectroscopic monitoring of the formation of [L3Pd(C(O)CH$_3$)Cl]
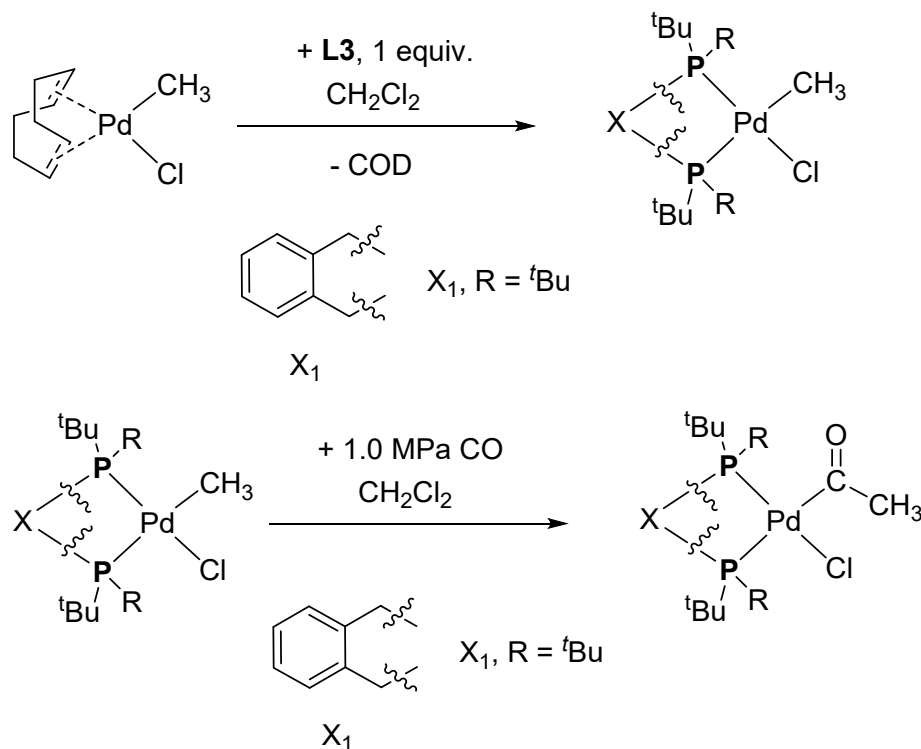
In the first step [**L3**Pd(CH3)Cl] was prepared from [(COD)Pd(CH$_3$)Cl] (Sigma-Aldrich) and **L3** (ABCR) via ligand substitution. All steps were performed under argon and the solvent used have been dried and was purged with argon. To a solution of the starting material [(COD)Pd(CH$_3$)Cl] (900 mg, 3.4 mmol) in dichloromethane (45 ml), the ligand **L3** (1.35 mg, 3.4 mmol) dissolved in dichloromethane (45 ml) was added slowly at room temperature. This mixture was stirred for 4h at room temperature. The solution was then concentrated to ca. 30 ml. For precipitation of the product-complex 90 ml of *n*-hexane was added. At first, precipitation did not occur readily, therefore the mixture was treated in vacuum to reduce the entire volume. The liquid filtrate was removed by canula and the solid product-complex was washed several times with *n*-hexane and at the end with *n*-pentane. Finally, the product-complex was dried under vacuum.

^{1}H NMR (300 MHz, CD$_2$Cl$_2$) δ 7.40 (m, 1H), 7.33 (m, 1H), 7.15 (m, 2H), 3.53 (s, broad, 2H), 3.34 (d, J(P,H) = 8.2 Hz, 2H), 1.46 (d, J(P,H) = 13.3 Hz, 36H), 1.10 (dd, J(P,H) = 6.9 Hz, J(P,H) = 2.8 Hz, 3H).
^{31}P NMR (122 MHz, CD$_2$Cl$_2$) Main complex: δ 49.57 (d, J(P,P) = 31.2 Hz), 18.75 (d, J(P,P) = 31.2 Hz); Impurities: δ 61.20 (s), 36.68 (s).
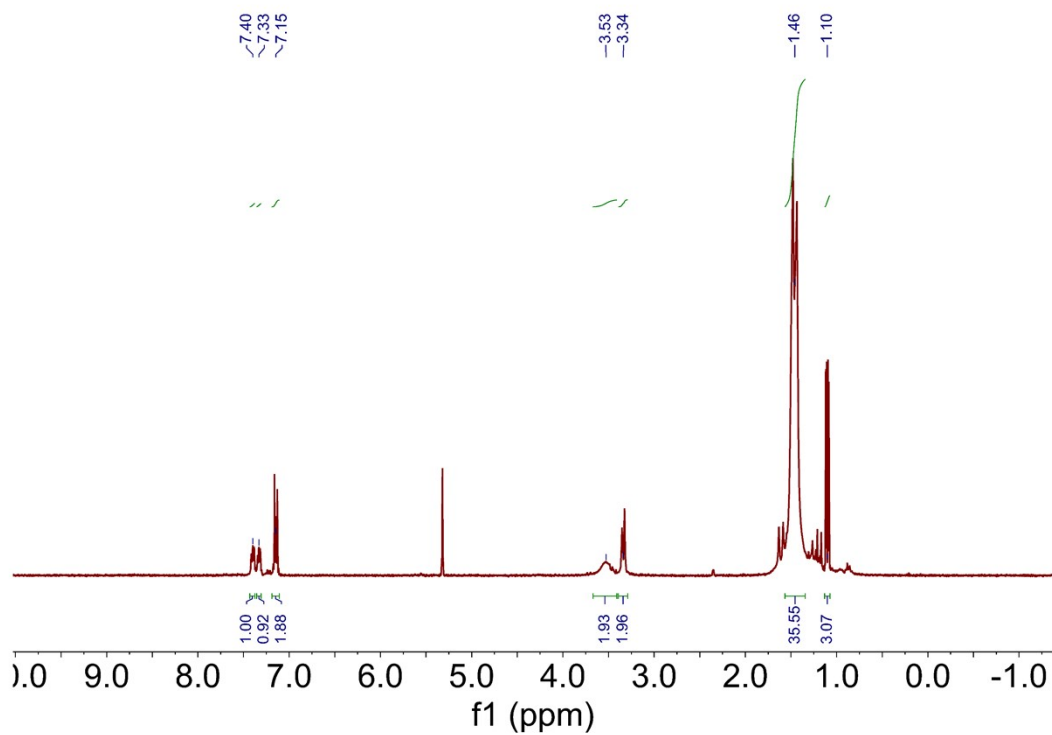
Figure SI-63 ^{1}H NMR spectrum for [**L3**Pd(CH$_3$)Cl] at 0.1 MPa of argon (297 K) in CD$_2$Cl$_2$.
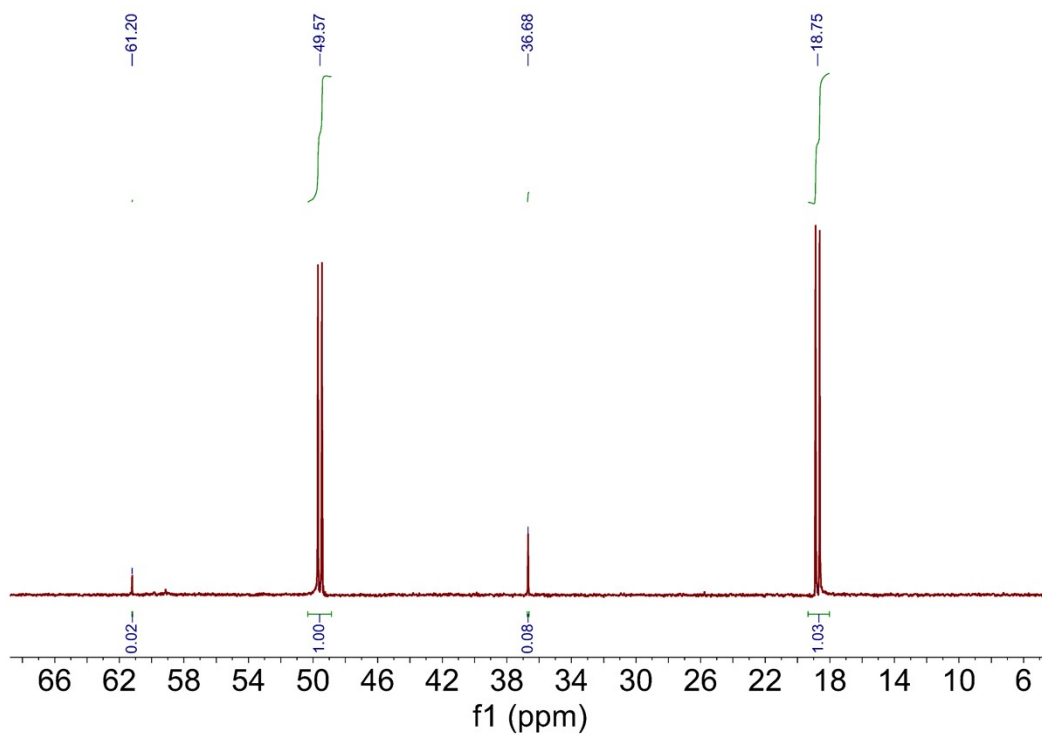
Figure SI-64 ^{31}P NMR spectrum for [**L3**Pd(CH$_3$)Cl] at 0.1 MPa of argon (297 K) in CD$_2$Cl$_2$.

For the HP in situ IR experiment, a solution of [**L3**Pd(CH$_3$)Cl] (99.3 mg, 0.18 mmol) in 6 ml dichloromethane (CH$_2$Cl$_2$) was prepared under argon to reach a Pd concentration of 30 mM. This solution was transferred into the HP FTIR apparatus described above. At θ = 30 °C, formation of [**L3**Pd(C(O)CH$_3$)Cl] was initiated by the addition of 1.0 MPa of CO, synchronized by the registration of IR-spectra. As a time-interval, we selected dt = 6 sec in order to monitor the formation-phase with a reasonable time-resolution. The formation of the acyl complex (ν(CO) = 1692 cm^{-1}) reached a plateau after ca. 30 sec. Also, a carbonyl band centered at 1937 cm^{-1} was observed which increased slightly in intensity. We did not perform any further experiments to assign this additional band.
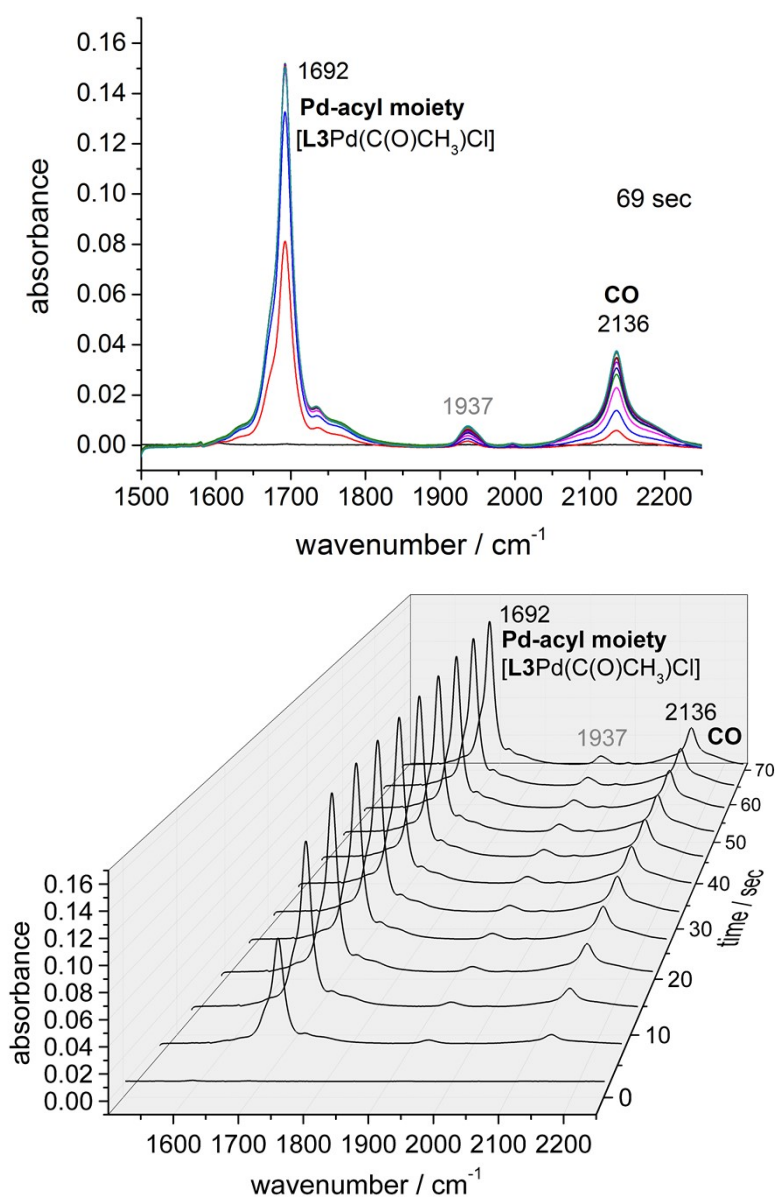
Figure SI-65 Different representations of a infrared spectra series collected during the formation of [**L3**Pd(C(O)CH$_3$)Cl] from [**L3**Pd(CH$_3$)Cl] at 1.0 MPa of CO. Conditions: θ = 30 °C, [Pd] = 30 mM, p(CO) = 1.0 MPa, solvent: CH$_2$Cl$_2$, registered time-span: ca. 69 sec. The band at ν(CO) = 1937 cm^{-1} stems from a not further characterized Pd-carbonyl complex.

NMR experiment on [L1Pd(OTs)](OTs) in the presence of ethene and carbon monoxide

To confirm the results obtained by FTIR-spectroscopy in which no significant amounts of an acyl complex could be identified when catalysts of the type [**L**Pd(OTs)](OTs) (**L**: **L1**, **L2**) ([Pd] = 30 mM) were exposed to ethene (1.0 MPa) and carbon monoxide (1.0 MPa), a similar HP NMR experiment was conducted for the system Pd/**L1** system.

To prevent the alcoholysis to take place in the presence of an alcohol, THF-d8 was used as a solvent.

The precatalyst [**L1**Pd(dba)] (δ(^{31}P)/ppm = 37.5 (s), 33.3 (s)) dissolved in THF-d8 in the presence of five equivalents of pTSA and two equivalents of benzochinone (BQ) was completely transformed into [**L1**Pd(OTs)](OTs) with δ(^{31}P) = 32.9 and -7.5 ppm at room temperature under 0.1 MPa of argon. The sample was filled into the 5 mm sapphire tube from Daedalus and 1.0 MPa of ethene was introduced after which the tube was thoroughly shaken to ensure a stationary gas concentration. As observed for the sample in methanol, no changes in the chemical shift values were observed. In a next step, the tube was additionally pressurized with 1.0 MPa of ^{12}CO. In this case also, the signal positions for the palladium complex remained unchanged. In a further step, an identical sample was prepared but this time we used 1.0 MPa of ^{13}CO. However, no alterations of the signal positions took place and no coupling between ^{31}P and ^{13}CO were visible.

In the ^{13}C spectrum at room temperature, also no signals assignable to Pd acyl complexes, for which resonance signals at around ≈230 ppm would be expected, could be found. A day later we started a series of NMR measurements cooling down to 219 K. None of the spectra showed any signals for an acyl complex. Also, the ^{31}P-spectra showed only small signal shifts and linewidth narrowing due to cooling. The doublet splitting of the signals for [**L1**Pd(OTs)](OTs) was observed at 233 K with ^{2}J(P,P) ≈ 8.4 Hz. At 193 K again line broadening was observed.

[(**L1**)Pd(OTs)]OTs, 297 K

1.0 MPa ethene
1.0 MPa ^{13}CO

1.0 MPa ethene
1.0 MPa ^{12}CO

1.0 MPa ethene

0.1 MPa argon

^{31}P{^{1}H}

60   40   20   0   -20   -40

ppm
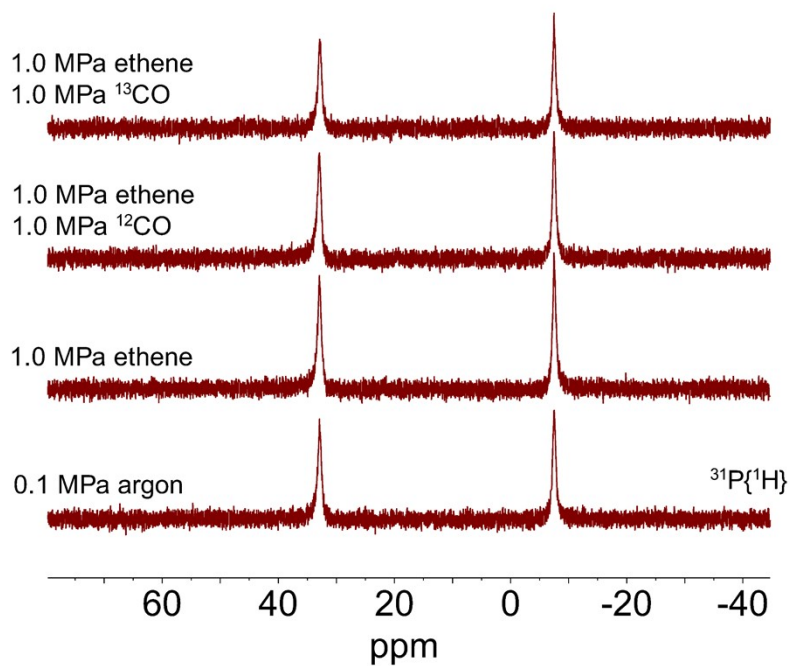
Figure SI-66 ^{31}P{^{1}H} NMR spectra of [**L1**Pd(OTs)(OTs)] (**1B'**) at different gas compositions. Conditions: T = 297 K, [Pd] = 30 mM, solvent: THF-d8. Signal positions at 0.1 MPa of Ar: Pd/**L1** (**1B'**) δ(^{31}P)/ppm = 32.9 (s), -7.5 (s).

[(**L1**)Pd(OTs)]OTs (**1B'**)

213 K

233 K

273 K

^{13}CO

297 K

^{13}C{^{1}H}

250   240   230   220   210   200   190   180

ppm
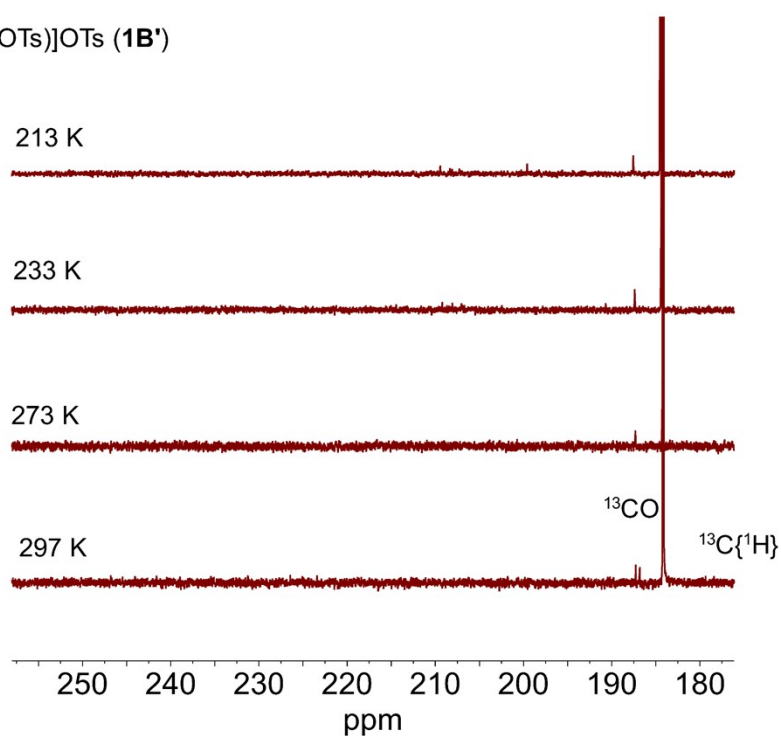
Figure SI-67 ^{13}C{^{1}H} NMR spectra of [**L1**Pd(OTs)(OTs)] (**1B'**) in the presence of ethene and ^{13}CO under varying temperature. Conditions: T = 297 K, [Pd] = 30 mM, p(C$_2$H$_4$)$_{ini}$= 1.0 MPa, p(^{13}CO)$_{ini}$= 1.0 MPa, solvent: THF-d8. Signal positions of ^{13}CO at 297 K: δ(^{13}C)/ppm = 184.2 (s).

[(**L1**)Pd(OTs)]OTs (**1B'**)
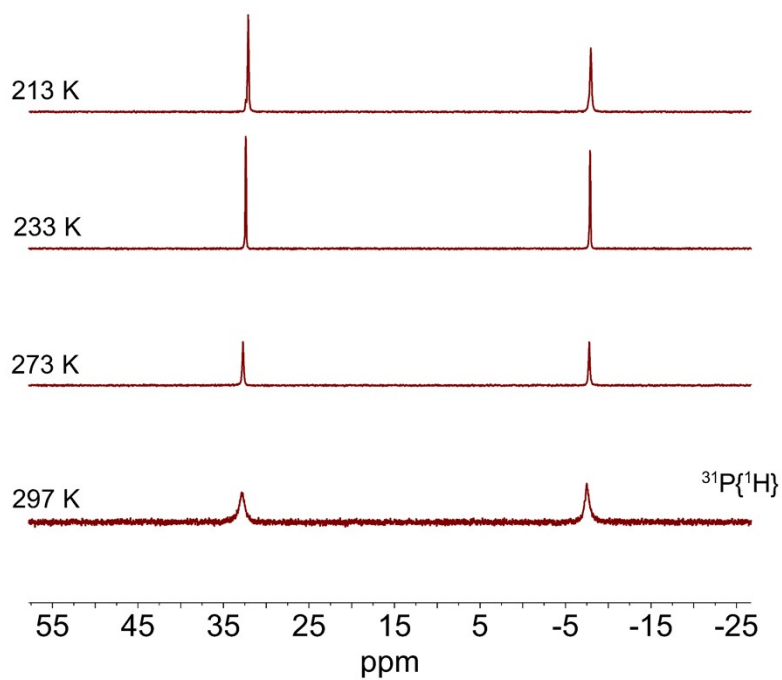
Figure SI-68 ^{31}P{^{1}H} NMR spectra of [**L1**Pd(OTs)(OTs)] (**1B'**) in the presence of ethene and ^{13}CO under varying temperature. Conditions: T = 297 K, [Pd] = 30 mM, p(C$_2$H$_4$)$_{ini}$= 1.0 MPa, p(^{13}CO)$_{ini}$= 1.0 MPa, solvent: THF-d8. Signal positions at 297 K: Pd/**L1** (**1B'**) δ(^{31}P)/ppm = 32.9 (s), -7.5 (s). Doublet splitting became observable at 233 K with ^{2}J(P,P) ≈ 8.4 Hz. At 193 K line broadening took place again.

SI-O: DFT computations

Computational methods and models

All calculations were carried out by using the Gaussian 09 program.[10] All structures were optimized at the M06L[11,12], B3LYP[13] and B3PW91[13,14] level of density functional theory (DFT) with the TZVP[15] basis set (LANL2DZ effective core potential for Pd and Fe) in gas phase and in dichloromethane by using the solvation model based on solute electron density (SMD)[16]. All optimized structures were characterized either as energy minimums without imaginary frequencies. The thermal correction to Gibbs free energy at 298 K from frequency analysis was added to the total electronic energy, and the corrected Gibbs free energy (ΔG) at 298 K was used for discussion and comparison. In all our calculations, we used the real-size model systems without constrains and simplifications for the Pd/**L1** and Pd/**L2** system. The optimized structures were displayed by the CYLview visualization program.[17]

M06L-SMD(CH$_2$Cl$_2$)/TZVP(LANL2DZ) level

For the Pd/**L1** and Pd/**L2** system at M06L-SMD(CH$_2$Cl$_2$)/TZVP(LANL2DZ) level, the pyridyl protonated isomer of **[H$_{py}$L1Pd(OTf)]** and **[H$_{py}$L2Pd(OTf)]** was most favorable species. The Pd hydride isomer of **[L1Pd-H(OTf)]** and **[L2Pd-H(OTf)]** was less favorable than pyridyl protonated isomer by 29 and 44 kJ/mol, respectively. The equilibrium constants K(**[H$_{py}$LPd(OTf)]**/**[LPd-H(OTf)]**) at 298 K was 1×10^5 and 5×10^7 for Pd/**L1** and Pd/**L2** system, respectively. This is also in good agreement with the experimental results that the nitrogen atom of the ligand was found protonated. Furthermore, it was found that the formation of **[H$_P$L1Pd(OTf)]** and **[H$_P$L2Pd(OTf)]** was endergonic by 50 and 21 kJ/mol, respectively. The equilibrium constants K(**[H$_{py}$LPd(OTf)]**/**[H$_P$L1Pd(OTf)]**) at 298 K was 6×10^8 and 5×10^3 for Pd/**L1** and Pd/**L2** system, respectively. This is consistent with our experimental results that the protonation of phosphous atom of the ligand was not observed.
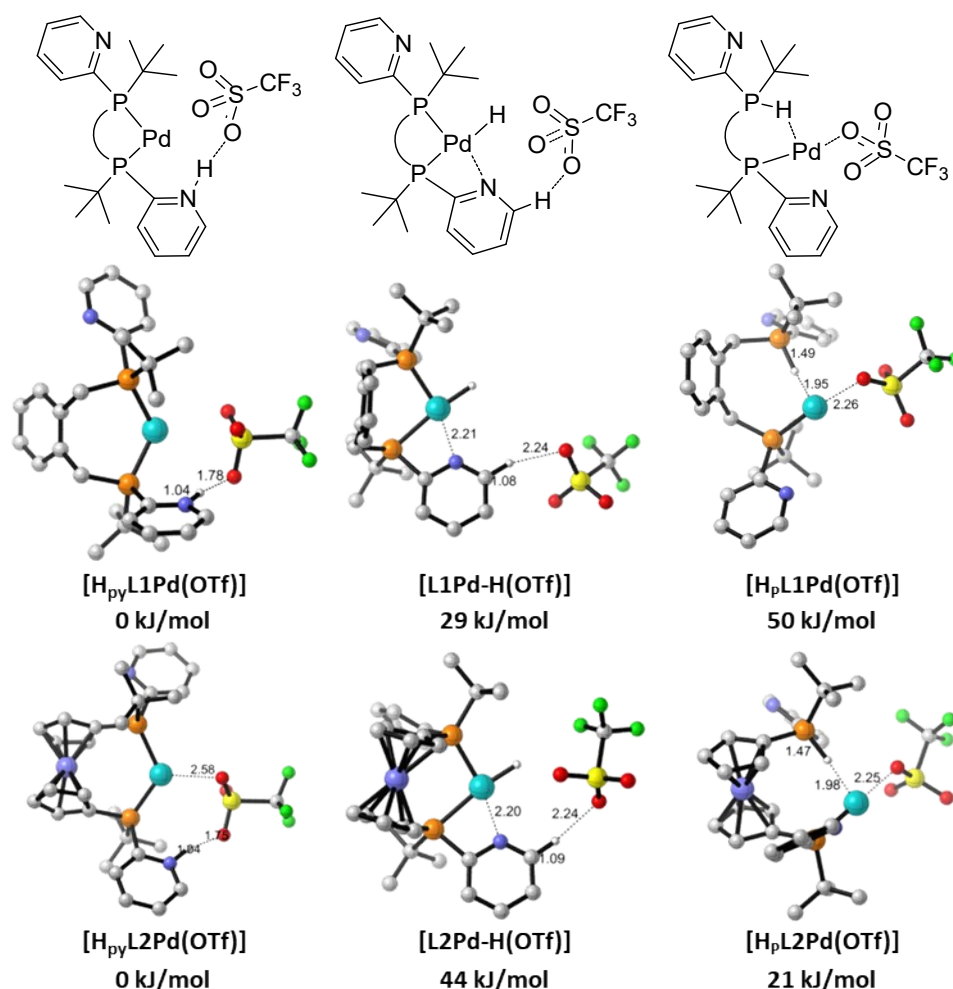
Figure SI-69   Optimized structures and Gibbs free energy for **[H$_{py}$LPd(OTf)]**, **[LPd-H(OTf)]** and **[H$_P$LPd(OTf)]** at M06L-SMD(CH$_2$Cl$_2$)/TZVP(LANL2DZ) level (only the hydrogens are omitted for clarity).

B3LYP-SMD(CH$_2$Cl$_2$)/TZVP(LANL2DZ) level

For the Pd/**L1** and Pd/**L2** system at B3LYP-SMD(CH$_2$Cl$_2$)/TZVP(LANL2DZ) level, it was found that the pyridyl protonated isomer of **[H$_{py}$L1Pd(OTf)]** and **[H$_{py}$L2Pd(OTf)]** was most favorable species. The Pd hydride isomer of **[L1Pd-H(OTf)]** and **[L2Pd-H(OTf)]** was less favorable than pyridyl protonated isomer by 10 and 11 kJ/mol, respectively. The equilibrium constants K(**[H$_{py}$LPd(OTf)]**/**[LPd-H(OTf)]**) at 298 K is 85 and 57 for Pd/**L1** and Pd/**L2** system, respectively. This is in agreement with the experimental results that the nitrogen atom of the ligand was found protonated. Furthermore, it was found that the formation of phosphorus protonated isomer **[H$_P$L1Pd(OTf)]** and **[H$_P$L2Pd(OTf)]** was highly endergonic by 54 and 27 kJ/mol, respectively. The equilibrium constants K(**[H$_{py}$LPd(OTf)]**/**[H$_P$L1Pd(OTf)]**) at 298 K was 3×10^9 and 5×10^4 for Pd/**L1** and Pd/**L2** system, respectively. This is consistent with our experimental results that the protonation of phosphous atom of the ligand was not observed.

[H$_{py}$L1Pd(OTf)]
0 kJ/mol

[L1Pd-H(OTf)]
10 kJ/mol

[H$_P$L1Pd(OTf)]
54 kJ/mol

[H$_{py}$L2Pd(OTf)]
0 kJ/mol

[L2Pd-H(OTf)]
11 kJ/mol

[H$_P$L2Pd(OTf)]
27 kJ/mol
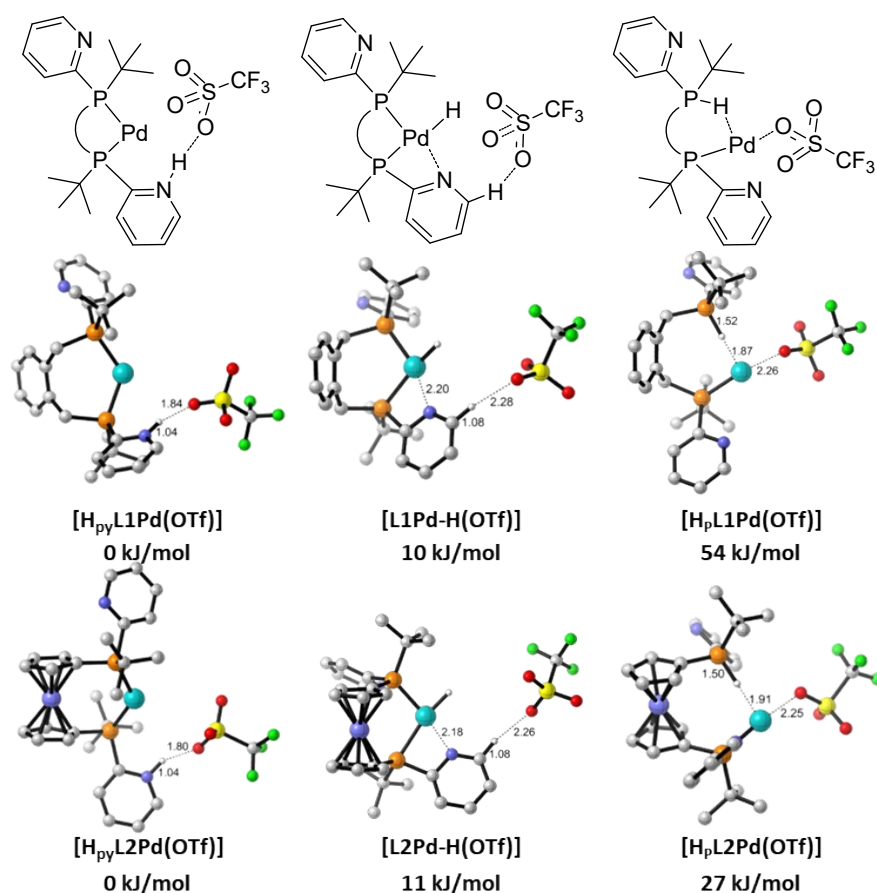
Figure SI-70   Optimized structures and Gibbs free energy for **[H$_{py}$L1Pd(OTf)]**, **[L1Pd-H(OTf)]** and **[H$_P$L1Pd(OTf)]** at B3LYP-SMD(CH$_2$Cl$_2$)/TZVP(LANL2DZ) level (only the hydrogens are omitted for clarity).

B3PW91-SMD(CH₂Cl₂)/TZVP(LANL2DZ) level

For the Pd/**L1** system at B3PW91-SMD(CH$_2$Cl$_2$)/TZVP(LANL2DZ) level, it was found that the Pd hydride **[L1Pd-H(OTf)]** was most favorable species, and the pyridyl protonated isomer of **[H$_{py}$L1Pd(OTf)]** was less favorable than Pd hydride **[L1Pd-H(OTf)]** by 6 kJ/mol. The equilibrium ratio between **[L1Pd-H(OTf)]** and **[H$_{py}$L1Pd(OTf)]** is 11:1 (298 K). For the Pd/**L2** system, the Pd hydride **[L2Pd-H(OTf)]** was found highly unfavorable than the pyridyl protonated isomer of **[H$_{py}$L2Pd(OTf)]** by 14 kJ/mol. The equilibrium constant K(**[H$_{py}$LPd(OTf)]**/**[H$_P$L1Pd(OTf)]**) at 298 K is 3×10^2 for Pd/**L2** system. This is in good agreement with the experimental results that the nitrogen atom of the pyridyl was found protonated. Besides, the possibility of the protonation of phosphous atom of the ligand was also calculated. It was found that the formation of **[H$_P$L1Pd(OTf)]** and **[H$_P$L1Pd(OTf)]** is highly endergonic by 55 and 39 kJ/mol, respectively. The equilibrium constants K(**[H$_{py}$LPd(OTf)]**/**[H$_P$L1Pd(OTf)]**) at 298 K was 4×10^9 and 7×10^6 for Pd/**L1** and Pd/**L2** system, respectively. This is consistent with our experimental results that the protonation of phosphous atom of the ligand was not observed.
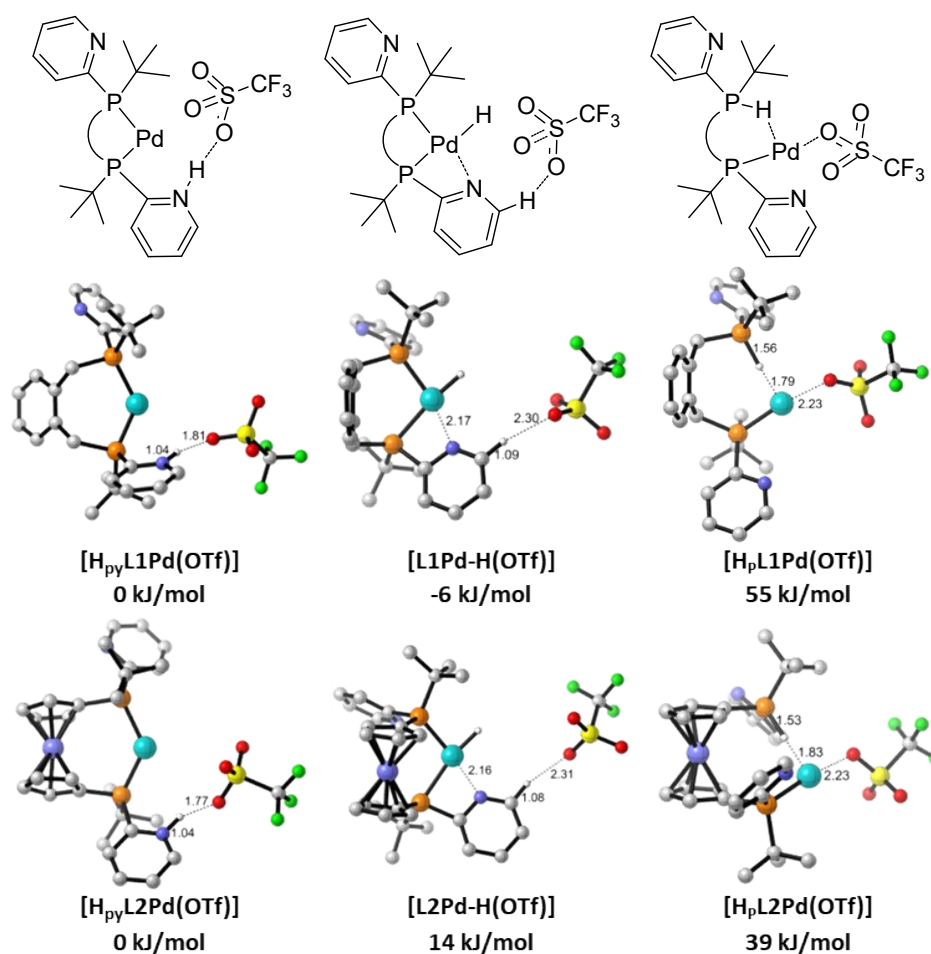
Figure SI-71 Optimized structures and Gibbs free energy for **[H$_{py}$L1Pd(OTf)]**, **[L1Pd-H(OTf)]** and **[H$_P$L1Pd(OTf)]** at B3PW91-SMD(CH$_2$Cl$_2$)/TZVP(LANL2DZ) level (only the hydrogens are omitted for clarity).

Comparing these three functional, it was found that the pyridyl protonated isomer of **[H$_{py}$L1Pd(OTf)]** and **[H$_{py}$L2Pd(OTf)]** are more stable than the Pd hydride isomer of **[L1Pd-H(OTf)]** and **[L2Pd-H(OTf)]** for functional of M06L and B3LYP. While, for functional B3PW91, the Pd hydride **[L1Pd-H(OTf)]** is in equilibrium with **[H$_{py}$L1Pd(OTf)]** for Pd/**L1** system, and the pyridyl protonated isomer of **[H$_{py}$L2Pd(OTf)]** is more favorable than **[L2Pd-H(OTf)]** for Pd/**L2** system.

Table SI-4 Computed Energetic Data for Optimized Structures

M06L-SMD(CH₂Cl₂)/TZVP(LANL2DZ)	B3LYP-SMD(CH₂Cl₂)/TZVP(LANL2DZ)	B3PW91-SMD(CH₂Cl₂)/TZVP(LANL2DZ)
[H$_{py}$L1Pd-OTf] E= -2892.759637 ZPE= 0.584781 NImag= 0 Htot = -2892.131775 Gtot = -2892.252632	**[H$_{py}$L1Pd-OTf]** E= -2893.000536 ZPE= 0.581327 NImag= 0 Htot = -2892.375136 Gtot = -2892.502613	**[H$_{py}$L1Pd-OTf]** E= -2892.252858 ZPE= 0.582475 NImag= 0 Htot = -2891.626751 Gtot = -2891.750233
[L1Pd-H(OTf)] E= -2892.74717 ZPE= 0.581539 NImag= 0 Htot = -2892.122745 Gtot = -2892.244027	**[L1Pd-H(OTf)]** E= -2892.99702 ZPE= 0.578719 NImag= 0 Htot = -2892.374937 Gtot = -2892.498768	**[L1Pd-H(OTf)]** E= -2892.250626 ZPE= 0.579224 NImag= 0 Htot = -2891.627932 Gtot = -2891.754851
[H$_P$L1Pd-OTf] E= -2892.739967 ZPE= 0.581751 NImag= 0 Htot = -2892.115501 Gtot = -2892.233415	**[H$_P$L1Pd-OTf]** E= -2892.97784 ZPE= 0.576881 NImag= 0 Htot = -2892.357085 Gtot = **-2892.482236**	**[H$_P$L1Pd-OTf]** E= -2892.226275 ZPE= 0.577305 NImag= 0 Htot = -2891.605038 Gtot = -2891.731465
[H$_{py}$L2Pd-OTf] E= -3092.499431 ZPE= 0.596098 NImag= 0 Htot = -3091.858126 Gtot = -3091.982534	**[H$_{py}$L2Pd-OTf]** E= -3092.664908 ZPE= 0.593192 NImag= 0 Htot = -3092.025515 Gtot = -3092.1553	**[H$_{py}$L2Pd-OTf]** E= -3091.93612 ZPE= 0.594174 NImag= 0 Htot = -3091.295815 Gtot = -3091.427005
[L2Pd-H(OTf)] E= -3092.482496 ZPE= 0.592253 NImag= 0 Htot = -3091.846151 Gtot = -3091.965756	**[L2Pd-H(OTf)]** E= -3092.657021 ZPE= 0.589603 NImag= 0 Htot = -3092.021462 Gtot = -3092.151296	**[L2Pd-H(OTf)]** E= -3091.92898 ZPE= 0.590929 NImag= 0 Htot = -3091.292289 Gtot = -3091.421722
[H$_P$L2Pd-OTf] E= -3092.48539 ZPE= 0.591749 NImag= 0 Htot = -3091.848192 Gtot = -3091.974597	**[H$_P$L2Pd-OTf]** E= -3092.648399 ZPE= 0.58851 NImag= 0 Htot = -3092.013602 Gtot = -3092.145044	**[H$_P$L2Pd-OTf]** E= -3091.9165 ZPE= 0.589336 NImag= 0 Htot = -3091.281011 Gtot = -3091.41222

Table SI-5 The Cartesian Coordinates (xyz) for Optimized Structures

M06L-SMD(CH₂Cl₂)/TZVP(LANL2DZ)	B3LYP-SMD(CH₂Cl₂)/TZVP(LANL2DZ)	B3PW91-SMD(CH₂Cl₂)/TZVP(LANL2DZ)
[H_pyL1Pd-OTf]	**[H_pyL1Pd-OTf]**	**[H_pyL1Pd-OTf]**
C -3.12899900 -2.06862000 0.00955700	C -3.62728900 -2.03874600 -0.35718300	C -3.57544000 -2.03949700 -0.33045200
C -2.78530400 -3.01310300 -0.95755100	C -3.29857700 -2.60360600 -1.59077000	C -3.24302700 -2.61373400 -1.55630700
H -1.76289400 -3.06211800 -1.31699600	H -2.28578800 -2.52643000 -1.96516500	H -2.23012500 -2.52731600 -1.93299400
C -3.75880600 -3.86891600 -1.44306300	C -4.28465300 -3.25608100 -2.32221600	C -4.22267700 -3.28524700 -2.27538300
H -3.51308400 -4.61572900 -2.18851000	H -4.05119900 -3.70430400 -3.28055300	H -3.98779600 -3.74277800 -3.23035600
C -5.05436900 -3.74111700 -0.96680200	C -5.57130900 -3.31656000 -1.80352100	C -5.50473700 -3.35362600 -1.75123600
H -5.85267600 -4.37817400 -1.32546800	H -6.37339000 -3.81045200 -2.33714700	H -6.30442700 -3.86296800 -2.27623500
C -5.31195500 -2.76428300 -0.01777000	C -5.81444000 -2.71560700 -0.57263800	C -5.74932100 -2.74097400 -0.52830500
H -6.31699300 -2.63035900 0.37255900	H -6.80923100 -2.73451400 -0.13901800	H -6.74367400 -2.76586300 -0.09060100
C -1.23477400 -1.84551300 2.22565800	C -2.02130000 -2.35546800 2.13238000	C -1.95810600 -2.31674300 2.13204000
C -0.12244300 -1.00832600 2.85424500	C -0.83539400 -1.80061800 2.93717200	C -0.77272500 -1.74753700 2.91568700
H 0.23689000 -1.49852700 3.76407500	H -0.63303600 -2.46198600 3.78576900	H -0.55211200 -2.40152800 3.76664200
H -0.46020700 -0.00781200 3.13717100	H -1.04079700 -0.80503300 3.33742200	H -0.98252700 -0.75043600 3.31228500
H 0.72284300 -0.90722800 2.16960600	H 0.06971100 -1.74295300 2.32891400	H 0.12391100 -1.68514000 2.29333400
C -2.37270300 -2.04084300 3.21732100	C -3.25172300 -2.46584400 3.04110700	C -3.17561500 -2.43056600 3.04712500
H -3.20766300 -2.59318500 2.78323800	H -4.13168700 -2.81410200 2.50022800	H -4.06006300 -2.77909200 2.51142500
H -2.75768200 -1.09179100 3.59350300	H -3.49851300 -1.51301200 3.51284500	H -3.41960700 -1.47795500 3.52277900
H -2.01520600 -2.60969600 4.08080700	H -3.04253700 -3.18183500 3.84329200	H -2.95929200 -3.14818200 3.84699400
C -0.66141500 -3.19473900 1.80466800	C -1.65164300 -3.74210300 1.58426900	C -1.58262000 -3.69539100 1.58426900
H -0.22661200 -3.69904200 2.67230400	H -1.36781400 -4.39691000 2.41401000	H -1.27848100 -4.34558100 2.41146600
H 0.12986600 -3.07617500 1.06041900	H -0.80481000 -3.69195300 0.89537600	H -0.74594000 -3.63599100 0.88204900
H -1.42735100 -3.85496100 1.39320400	H -2.48819900 -4.21191500 1.06334300	H -2.42227700 -4.17552700 1.07608900
C -2.78529700 0.47431600 1.33022700	C -3.16216100 0.30430800 1.35911200	C -3.13607200 0.30452400 1.35534100
H -3.69646000 0.06714600 1.77259900	H -4.09098100 -0.03535400 1.81710200	H -4.06340000 -0.04513000 1.81300500
H -2.18294600 0.89240400 2.13853500	H -2.50582700 0.65029100 2.15836500	H -2.48507000 0.66655200 2.15404500
C -3.14317500 1.51915100 0.31582100	C -3.47637100 1.41801800 0.38472600	C -3.45797300 1.39763900 0.36950600
C -4.36516500 1.38119100 -0.34921200	C -4.73301000 1.37403300 -0.23843800	C -4.70790500 1.33173200 -0.25652900
H -4.97759700 0.51758800 -0.11452200	H -5.38461000 0.53827000 -0.01689300	H -5.35231300 0.49011400 -0.02446500
C -4.80910800 2.31052200 -1.27348500	C -5.16889600 2.36393100 -1.10743000	C -5.15240000 2.30415600 -1.13862800
H -5.76208000 2.17017100 -1.76958700	H -6.14783300 2.29038900 -1.56630900	H -6.12971800 2.21385800 -1.60074900
C -4.03448600 3.42950100 -1.54707900	C -4.34728400 3.45638100 -1.36051400	C -4.34310700 3.40116400 -1.40133400
H -4.37304600 4.18011800 -2.24479600	H -4.67288500 4.25422800 -2.01747400	H -4.67528900 4.18866400 -2.06932100
C -2.82336000 3.58640100 -0.88796700	C -3.10472400 3.52445900 -0.74677700	C -3.10553300 3.49040300 -0.78401300
H -2.22378800 4.46994300 -1.08136900	H -2.47971400 4.39014100 -0.92733900	H -2.48812100 4.36191800 -0.97132200
C -2.34416800 2.64392500 0.02523100	C -2.63166000 2.52026200 0.11028400	C -2.62540500 2.50283100 0.08462200
C -1.01378200 2.89348800 0.67614100	C -1.27285100 2.73555200 0.74326100	C -1.27693300 2.73770900 0.71944900
H -0.97205400 2.41607600 1.65725400	H -1.23602200 2.28586700 1.73595100	H -1.24275100 2.30577500 1.72207700
H -0.86272200 3.96418700 0.82973700	H -1.10115400 3.80604000 0.86236800	H -1.11089900 3.81275500 0.81841500
C 1.71376000 2.25884200 1.09217500	C 1.50441900 2.21108100 1.18270500	C 1.48170400 2.20965900 1.17427600
C 1.67546300 3.04846900 2.23359800	C 1.50706100 3.20744900 2.15147100	C 1.47656800 3.20435700 2.14212100
H 0.85763100 3.74113300 2.37332200	H 0.71803800 3.94369900 2.16549300	H 0.68166200 3.93659700 2.15495100
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H 2.64147800 3.57134900 4.07090200	H 2.51714500 4.04614700 3.84869100	H 2.47957300 4.04727800 3.84077000
C 3.73211200 2.06553000 3.00175100	C 3.54685900 2.32249500 3.08201300	C 3.51704000 2.33023400 3.07172800
H 4.52318900 1.96458600 3.72983200	H 4.35040400 2.34070500 3.80442300	H 4.32116300 2.35077200 3.79520200
C 3.74991600 1.29662100 1.86201600	C 3.51795000 1.33909400 2.11556500	C 3.49230300 1.34880100 2.10510500
H 4.51939300 0.57352700 1.63126600	H 4.25924800 0.55537700 2.01960500	H 4.23739900 0.56652900 2.00861300
C 1.07283200 3.49206000 -1.44784400	C 0.81281100 3.16288200 -1.51273600	C 0.80204200 3.14465800 -1.50652000
C 2.54724100 3.20214900 -1.71121300	C 2.25857500 2.77839000 -1.86280500	C 2.24253500 2.75678800 -1.84735500
H 2.71677700 2.15289100 -1.96713400	H 2.35259900 1.71761600 -2.10516000	H 2.33519900 1.69176000 -2.07600900
H 3.17821200 3.45452300 -0.85658200	H 2.95760800 3.01231000 -1.05749600	H 2.94039300 3.00127100 -1.04304000
H 2.89147300 3.80344200 -2.55611600	H 2.57240900 3.34671500 -2.74334200	H 2.55886200 3.31355800 -2.73539100
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H 1.38591700 5.03141500 0.06632200	H 1.38267600 4.84354900 -0.23051600	H 1.37009100 4.82201700 -0.22787000
H -0.13999300 5.18857600 -0.81167700	H -0.25524300 4.97487700 -0.88790300	H -0.26774500 4.95348600 -0.88973100
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C 0.29230600 3.31441100 -2.74741200	C -0.07355400 2.91348400 -2.73285800	C -0.07862200 2.88689400 -2.73285500
H 0.62845800 4.05117200 -3.48196200	H 0.27084100 3.54811500 -3.56630700	H 0.26082300 3.52216300 -3.55792500
H -0.78121100 3.44863000 -2.60962000	H -1.12148300 3.14729500 -2.55666200	H -1.12956600 3.11209400 -2.54557200
H 0.45074900 2.32085600 -3.17073400	H -0.01354700 1.87367900 -3.07197700	H -0.00992300 1.84516900 -3.05678800
C 4.08540600 -2.94752500 -1.08574800	C 5.47244400 -1.80191900 -1.48456900	C 5.39978300 -1.80632600 -1.48920300
F 4.32624600 -2.93109100 -2.39879800	F 4.81038900 -2.23758100 -2.56672500	F 4.72247800 -2.23358700 -2.55866900
F 3.76703900 -4.19575200 -0.73491200	F 6.55572200 -2.57548900 -1.31731500	F 6.46843500 -2.59272800 -1.32938300
F 5.21390900 -2.61206400 -0.45080500	F 5.88867500 -0.54821300 -1.72715400	F 5.82960000 -0.56400800 -1.73673800
N -4.38027200 -1.94475800 0.47322000	N -4.87225300 -2.09066600 0.13895900	N -4.81466000 -2.09801700 0.17151700
N 2.76279200 1.41139900 0.96562500	N 2.51632300 1.31125200 1.22135900	N 2.49450900 1.31652900 1.21293100
O 1.56635200 -2.22757300 -1.45696200	O 3.98871800 -3.28670500 0.16816700	O 3.91634900 -3.25941800 0.17335000
O 3.28621300 -0.44501700 -1.06020000	O 3.24219600 -0.93891200 -0.32428800	O 3.20370400 -0.91138400 -0.31828600
O 2.57843200 -1.91222700 0.82806500	O 5.24030200 -1.32378000 1.13368300	O 5.20147400 -1.32021500 1.11835300
P -1.78778700 -0.94606900 0.64074100	P -2.27069200 -1.19355900 0.62192100	P -2.22950500 -1.17373600 0.62905100
P 0.43513800 2.13664600 -0.25082800	P 0.20476300 1.93886900 -0.15080000	P 0.19241100 1.93530200 -0.15394300
Pd -0.05775200 -0.03691100 -0.59301000	Pd -0.40135400 -0.25377500 -0.38574000	Pd -0.39489800 -0.23582600 -0.38221100
S 2.70431900 -1.75692300 -0.63745700	S 4.36421400 -1.85867700 0.05569000	S 4.31244400 -1.84320000 0.05276600
H 2.80263300 0.78052400 0.14141000	H 2.54368400 0.53307000 0.53924200	H 2.52624500 0.53535200 0.52995700
[L1Pd-H(OTf)]	**[L1Pd-H(OTf)]**	**[L1Pd-H(OTf)]**
Pd 0.42553700 -0.18701100 0.19952000	Pd 0.21887800 0.11379900 0.03873700	Pd 0.29311800 0.08800400 -0.01840600
P 1.27172700 1.54628900 -1.20638300	P 1.85635100 1.66141800 -0.89820400	P 1.86144000 1.69250700 -0.87900300
P 2.36438000 -1.20701200 0.68728400	P 1.50021100 -1.72430000 0.44664200	P 1.62100000 -1.66891900 0.45051400
C 3.71994100 0.07059100 0.69103900	C 3.23265100 -1.11171700 0.88407600	C 3.30874300 -0.98935300 0.90489300
H 4.62747900 -0.40784600 1.06268300	H 3.80311600 -1.96488800 1.24847500	H 3.91704400 -1.81857500 1.26858100
H 3.89227400 0.26639200 -0.37002600	H 3.65847300 -0.84466500 -0.08238700	H 3.72769800 -0.69621900 -0.05930700
C 2.65191900 2.61222700 -0.61524000	C 3.44305200 1.86887000 0.55561300	C 3.41001300 1.98743200 0.09010500
H 3.53296100 2.30153700 -1.18396000	H 4.18533100 1.29644200 -0.50659000	H 4.19319200 1.45272800 -0.45577100
H 2.45554100 3.65104000 -0.88413600	H 3.75641100 2.91166000 0.02574600	H 3.66933900 3.04661600 0.06178500
C 3.72013600 1.36032200 2.82254000	C 3.39933200 -0.27956200 3.23193000	C 3.41005800 -0.16121700 3.25321300

C	3.44959800	2.46992600	3.60627200	C	3.47300900	0.70065600	4.21323100	C	3.43192600	0.81744100	4.23593100
C	2.87685300	3.59096100	3.02690800	C	3.48093700	2.03922200	3.84097800	C	3.38929200	2.15437100	3.86723400
C	2.61433900	3.59394100	1.66691300	C	3.44364600	2.36928100	2.49224400	C	3.35472600	2.48516100	2.52064300
C	2.89239600	2.48874700	0.86330900	C	3.37596300	1.39363200	1.49088400	C	3.33851300	1.51086500	1.51899100
C	3.42588700	1.32876700	1.45972100	C	3.31966500	0.03313900	1.87028800	C	3.33227700	0.15042300	1.89333300
H	4.18094600	0.48798300	3.27296100	H	3.40756700	-1.32180100	3.52670400	H	3.46086800	-1.20405700	3.54626300
H	3.68931600	2.45767000	4.66225500	H	3.52851800	0.41815700	5.25762900	H	3.48827600	0.53419900	5.28129200
H	2.65165900	4.46546700	3.62454000	H	3.53523900	2.82052200	4.58948100	H	3.40348000	2.93633500	4.61857400
H	2.19717800	4.48024100	1.20040300	H	3.48521900	3.41217400	2.19976900	H	3.35957800	3.53047900	2.22906500
C	2.89124100	-2.30511900	-0.69694800	C	1.82928400	-2.70636500	-1.10026600	C	2.00816700	-2.67013700	-1.05982900
C	1.93238100	-2.96232900	-1.46254500	C	0.88079900	-2.74016400	-2.12201000	C	1.07035700	-2.76486900	-2.08495800
N	4.20582800	-2.41046600	-0.91987200	N	2.99647800	-3.35700500	-1.17378200	N	3.19888900	-3.27290500	-1.10520600
C	2.35850000	-3.77454600	-2.50034400	C	1.15409500	-3.49210900	-3.25888700	C	1.38177800	-3.53366600	-3.19807500
H	0.87862100	-2.82653500	-1.24482500	H	-0.04559600	-2.18896200	-2.02630100	H	0.12198300	-2.24604000	-2.00736700
C	4.59783300	-3.19181000	-1.92812400	C	3.25222800	-4.06968600	-2.27479100	C	3.48986000	-4.00086400	-2.18378700
C	3.71807500	-3.89170600	-2.73972800	C	2.36340700	-4.17043000	-3.33977200	C	2.61591100	-4.16457500	-3.25117500
H	1.63922200	-4.30151900	-3.11513100	H	0.43522800	-3.54106800	-4.06761200	H	0.67168200	-3.63228500	-4.01163900
H	5.66914300	-3.25723900	-2.09040600	H	4.20838300	-4.58115300	-2.30298100	H	4.46715100	-4.47453300	-2.19251900
H	4.09493300	-4.50954300	-3.54450500	H	2.61975000	-4.76362000	-4.20818300	H	2.90322700	-4.77029000	-4.10254600
C	2.47934600	-2.28769000	2.23150000	C	0.90142400	-3.01241200	1.72687300	C	1.03720000	-2.93829600	1.73518100
C	1.79941300	-1.57719400	3.39647100	C	0.38366400	-2.28694800	2.97644700	C	0.47033800	-2.20310500	2.95039600
H	2.25098200	-0.61221600	3.62337700	H	1.15622000	-1.69558300	3.46640900	H	1.21174000	-1.57339100	3.44295800
H	0.74023200	-1.41388500	3.19465700	H	-0.45127600	-1.62785800	2.73735500	H	-0.38023500	-1.57705500	2.67385100
H	1.87997400	-2.20150000	4.28934900	H	0.03107800	-3.03581800	3.69159000	H	0.12412900	-2.94590500	3.67616400
C	1.72938000	-3.58143000	1.92816700	C	-0.25637700	-3.79383700	1.08630500	C	-0.07839000	-3.76117300	1.08644500
H	1.65078700	-4.16889200	2.84528500	H	-0.68948600	-4.45343700	1.84326000	H	-0.51095600	-4.41813700	1.84725100
H	0.71388600	-3.38625600	1.57530400	H	-1.04970200	-3.13281800	0.73185200	H	-0.88174500	-3.12748800	0.70216200
H	2.24271900	-4.19332500	1.18549300	H	0.07588800	-4.41621600	0.25454500	H	0.29017500	-4.38980100	0.27367800
C	3.93957400	-2.58705900	2.55138300	C	2.03199500	-3.98004000	2.10649600	C	2.18401000	-3.86048200	2.15273200
H	3.98495200	-3.30902100	3.36995200	H	1.61976900	-4.75714600	2.75657900	H	1.78284500	-4.63700200	2.81171900
H	4.46843200	-3.01793200	1.69914700	H	2.46861700	-4.47008200	1.23577100	H	2.64932000	-4.35628800	1.29839000
H	4.48120500	-1.69625200	2.87182900	H	2.83075600	-3.48248500	2.65825100	H	2.95926500	-3.32979400	2.70797100
C	-0.32915900	2.34236800	-0.78206000	C	0.60675600	2.89864300	-0.29525700	C	0.53855300	2.86219500	-0.32588000
C	-0.78722400	3.63731900	-0.92270200	C	0.65643500	4.27345700	-0.13504800	C	0.51164500	4.23411800	-0.15415400
N	-1.09175800	1.36465000	-0.23002000	N	-0.51096900	2.18716300	-0.00105000	N	-0.54781700	2.09042600	-0.08408700
C	-2.08327700	3.92406500	-0.50954000	C	-0.48851300	4.92948600	0.31486400	C	-0.68299900	4.82343100	0.25055100
H	-0.14811800	4.40141100	-1.34654800	H	1.56033000	4.82234000	-0.36106000	H	1.39646300	4.83064500	-0.33581300
C	-2.33542500	1.63993300	0.16018100	C	-1.61147500	2.81303500	0.42334100	C	-1.69422700	2.65219600	0.29729300
C	-2.86639600	2.91503900	0.02271000	C	-1.63474200	4.19471700	0.58519600	C	-1.79734200	4.02763500	0.46598300
H	-2.47641500	4.92806800	-0.60894700	H	-0.48294300	6.00435400	0.44695300	H	-0.74026200	5.89695800	0.39107000
H	-2.91025200	0.82783700	0.59200200	H	-2.47806600	2.19609700	0.62983500	H	-2.53608700	1.98980700	0.47010500
H	-3.88185600	3.10445500	0.34470700	H	-2.54148400	4.67584400	0.92696100	H	-2.74284900	4.45694300	0.77355200
C	1.38701700	1.44338000	-3.07485000	C	2.22983100	2.06152300	-2.71756700	C	2.22874800	2.07125900	-2.68960500
C	2.62566800	0.60884500	-3.39539600	C	3.03595100	0.88006700	-3.28026800	C	3.17154700	0.97724100	-3.19871400
H	3.54654700	1.07843500	-3.04472600	H	3.99714300	0.75611600	-2.77717900	H	4.14848600	1.01117100	-2.71085400
H	2.56368500	-0.39124100	-2.96102400	H	2.48139900	-0.05702100	-3.20280800	H	2.74799100	-0.02041700	-3.06054000
H	2.71241100	0.49383600	-4.47805200	H	3.24096000	1.06223600	-4.33896600	H	3.33632800	1.12479700	-4.27054000
C	1.49408100	2.82659100	-3.70204100	C	3.02388700	3.36535200	-2.86745300	C	2.86909500	3.44685100	-2.86571900
H	1.55481000	2.72747600	-4.78853000	H	3.20656000	3.54883900	-3.93070300	H	3.06738500	3.61255500	-3.92981500
H	0.62210200	3.44313200	-3.47941300	H	2.47786800	4.22487900	-2.47535100	H	2.21220700	4.24996600	-2.52558700
H	2.38722100	3.35955400	-3.37308400	H	3.99525800	3.31591300	-2.37196100	H	3.82142600	3.52742400	-2.33695400
C	0.13361900	0.72382800	-3.56254400	C	0.88670800	2.16295000	-3.44567900	C	0.89840500	1.99664200	-3.44201300
H	-0.77229300	1.29961000	-3.36532700	H	0.29612000	3.01628400	-3.11765800	H	0.20749400	2.78401600	-3.13251400
H	0.19975500	0.57087000	-4.64188800	H	1.07740900	2.29130300	-4.52387900	H	1.08778000	2.12214300	-4.51261200
H	0.02072300	-0.25593700	-3.09253800	H	0.28524100	1.26033900	-3.32743800	H	0.40404100	1.03220100	-3.29878700
H	-0.32164600	-1.18257300	1.19593400	H	-0.93875200	-0.63010000	0.77600400	H	-0.85134400	-0.73210900	0.65516600
O	-5.37228500	0.45375700	-0.86690600	O	-4.45606100	-0.26570300	-1.43545600	O	-4.69297300	-0.37420200	-1.47552200
S	-5.76590900	-0.01551300	0.48145900	S	-5.25491200	0.43527200	-0.39454300	S	-5.42554600	0.33779700	-0.40147100
C	-6.55758200	-1.68417300	0.12678700	C	-6.13691300	-0.99273900	0.49731600	C	-6.31270200	-1.06036200	0.50761000
O	-6.86308900	0.73912400	1.12587000	O	-6.38279300	1.25963100	-0.90326200	O	-6.54012000	1.20087700	-0.85769300
O	-4.63568800	-0.37771100	1.37265300	O	-4.45777000	1.06001200	0.69900700	O	-4.56861600	0.92493300	0.66025900
F	-5.69594900	-2.51113000	-0.48088900	F	-5.25124800	-1.85025900	1.03577000	F	-5.43741100	-1.94493700	1.00454500
F	-7.62548500	-1.55097500	-0.67115200	F	-6.91447900	-1.68750800	-0.35219300	F	-7.13941700	-1.72030300	-0.31451000
F	-6.96519600	-2.27735600	1.25578300	F	-6.92009500	-0.53484700	1.49010100	F	-7.04042800	-0.58662700	1.52768700

[H$_P$L1Pd-OTf]

C	-3.69894700	-1.26856300	0.32770000	C	-3.59975500	-1.47141300	0.06634200	C	3.49240100	1.40575700	0.21767800
C	-4.97500900	-0.72549100	0.45701900	C	-4.94839000	-1.16221500	0.25891700	C	4.84545400	1.07878000	0.30362700
H	-5.11397000	0.31008100	0.73996800	H	-5.24422900	-0.30290300	0.84393400	H	5.16358400	0.12539000	0.70542300
C	-6.07876900	-1.52898800	0.21787700	C	-5.91976500	-1.97379300	-0.31600900	C	5.79103700	1.99478200	-0.13743600
H	-7.07936300	-1.12312200	0.30609800	H	-6.97070700	-1.74743200	-0.18075200	H	6.84847600	1.75942000	-0.08246600
C	-5.87950100	-2.85359800	-0.12984900	C	-5.52049400	-3.07449500	-1.06226100	C	5.35996200	3.21059500	-0.64594200
H	-6.71164200	-3.51675900	-0.32778200	H	-6.24155300	-3.73316100	-1.52931600	H	6.06113000	3.95548000	-1.00362700
C	-4.57537800	-3.31678300	-0.22201900	C	-4.15789000	-3.31357500	-1.19879200	C	3.99347600	3.45405400	-0.69000100
H	-4.37615900	-4.35079000	-0.48710100	H	-3.80135300	-4.16328000	-1.77159000	H	3.61263300	4.39370900	-1.08000000
C	-1.94505900	-0.48198800	2.53012400	C	-2.23715000	-0.95558800	2.66952200	C	2.24019100	0.44172000	2.71002900
C	-0.64649300	0.22195200	2.91639900	C	-1.05807800	-0.24869200	3.35630800	C	1.07129000	-0.34570500	3.30665900
H	-0.48913100	0.14531300	3.99582500	H	-1.02502800	-0.54475800	4.40935400	H	1.08887000	-0.24656100	4.39737100
H	-0.65453400	1.28715200	2.66877500	H	-1.15159400	0.83942100	3.32625700	H	1.12460700	-1.41287400	3.07434000
H	0.21058300	-0.23712200	2.41682100	H	-0.10754500	-0.52526300	2.89644200	H	0.11363400	0.03799000	2.94607400
C	-3.12196600	0.13679200	3.27117000	C	-3.54507200	-0.55773700	3.36470100	C	3.55707300	-0.07995700	3.28058100
H	-4.06985800	-0.32923300	2.99561300	H	-4.41055500	-1.06515000	2.93733500	H	4.42039600	0.46075000	2.88812500
H	-3.20533700	1.21050600	3.09556900	H	-3.72438900	0.51859800	3.33494800	H	3.69998400	-1.14668900	3.09329900
H	-2.99386500	-0.00415100	4.34787700	H	-3.48798600	-0.84826500	4.41874000	H	3.55361800	0.06047300	4.36703000
C	-1.82808300	-1.96301000	2.87459000	C	-2.04058400	-2.47544000	2.77557700	C	2.07447700	1.92229400	3.06138300
H	-1.61707600	-2.07715000	3.94121800	H	-1.96763100	-2.75645000	3.83085500	H	2.00961300	2.02913200	4.14697400
H	-1.01709100	-2.43864100	2.31648900	H	-1.12456500	-2.70790400	2.22542400	H	1.16210000	2.33757400	2.62449700
H	-2.74806300	-2.50908100	2.66030900	H	-2.87630800	-3.02864700	2.34268400	H	2.91988900	2.52282900	2.71780900
C	-2.59064200	1.45812700	0.45713100	C	-2.77606500	1.29296200	0.80204800	C	2.73037700	-1.43741700	0.46815300
H	-3.59802200	1.60622800	0.84986000	H	-3.78911300	1.31516900	1.20434400	H	3.76925900	-1.50209200	0.79689100
H	-1.92883700	1.98963100	1.14127400	H	-2.14143000	1.78656600	1.53711800	H	2.15334400	-2.07410800	1.14019300
C	-2.49971200	2.00997800	-0.93291800	C	-2.76285500	2.03516700	-0.51466700	C	2.63202200	-1.91631200	-0.95640600

C	-3.47992700	1.65810400	-1.86444000
H	-4.26957900	0.98122600	-1.55657900
C	-3.47294700	2.15449400	-3.15582900
H	-4.24788400	1.85869800	-3.85258100
C	-2.47682300	3.03735000	-3.54560900
H	-2.46383100	3.44431700	-4.55056400
C	-1.49845200	3.39992600	-2.63838600
H	-0.71748300	4.09331800	-2.93355700
C	-1.48251600	2.89185100	-1.33847200
C	-0.38287700	3.34076600	-0.41696800
H	-0.73862200	3.56073600	0.59176200
H	0.07949400	4.25917800	-0.78178700
C	1.86121600	2.58049600	1.32434000
C	2.60384200	1.61782400	2.00191700
H	2.66713900	0.60039100	1.62803300
C	3.24094400	1.99806100	3.17178500
H	3.82728100	1.27979100	3.73115500
C	3.10823300	3.30459300	3.61254300
H	3.58768000	3.64028000	4.52283300
C	2.33539200	4.18531800	2.86890200
H	2.20585800	5.21350000	3.19129100
C	2.11307400	2.02645300	-1.65136700
C	3.34043200	1.23429600	-1.20548400
H	3.06810400	0.27462500	-0.76204000
H	3.94983100	1.78757800	-0.48997400
H	3.95887800	1.02853000	-2.08129800
C	2.50529100	3.42872200	-2.09878700
H	2.95761100	4.00520900	-1.28920900
H	1.65309500	3.98945800	-2.48620000
H	3.24098600	3.35255700	-2.90208700
C	1.38885800	1.26563900	-2.76119300
H	2.07895200	1.12307400	-3.59546700
H	0.51858200	1.80350300	-3.13535600
H	1.06197200	0.27860700	-2.42203800
C	3.99446500	-3.06876600	-0.96713900
F	4.61197600	-2.00714000	-1.49398700
F	3.69177000	-3.91160900	-1.95575900
F	4.84943500	-3.68064100	-0.14323700
N	-3.50488100	-2.55314700	-0.01072400
N	1.71412100	3.84425900	1.74026600
O	1.66154300	-1.92456100	-1.15663400
O	2.97033600	-1.56792500	0.95313200
O	1.90444100	-3.79873200	0.49969200
P	-2.11686400	-0.34421000	0.63720100
P	0.96380300	2.12099500	-0.18973600
Pd	-0.27544500	-1.04463300	-0.39914200
S	2.45386100	-2.54157100	-0.03388600
H	0.39316600	0.75416700	-0.04606100

C	-3.84682500	1.85908700	-1.38665300
H	-4.62715500	1.16118400	-1.11345400
C	-3.96153000	2.56178100	-2.57760100
H	-4.81518800	2.39440500	-3.22343300
C	-2.98844500	3.49545100	-2.91953000
H	-3.07051100	4.07042800	-3.83339700
C	-1.91273300	3.69163800	-2.06659800
H	-1.16385700	4.43267400	-2.31973600
C	-1.76708400	2.96687300	-0.87686100
C	-0.57382200	3.28723400	-0.00626300
H	-0.81006200	3.20517100	1.05462000
H	-0.24436900	4.31220200	-0.17281200
C	1.97742200	2.57262500	1.25263600
C	2.74503800	1.57063100	1.84200900
H	2.75044700	0.56053200	1.45179800
C	3.51314400	1.90538400	2.95306600
H	4.12323500	1.15326400	3.43763100
C	3.48046700	3.20966300	3.42658300
H	4.06120600	3.50909400	4.28953800
C	2.67646600	4.13756700	2.77046700
H	2.62351300	5.16487700	3.11377000
C	1.89471500	2.52563200	-1.80048300
C	3.24943900	1.81232200	-1.66505800
H	3.13400100	0.74353800	-1.47830000
H	3.86571500	2.24273300	-0.87505000
H	3.78836900	1.92714300	-2.60912000
C	2.10978200	4.03224700	-2.00067200
H	2.64902500	4.48298500	-1.16550500
H	1.17028000	4.56908000	-2.13611900
H	2.70957200	4.17868900	-2.90336500
C	1.11320800	1.91599900	-2.97562200
H	1.70720700	2.04216500	-3.88484500
H	0.15141000	2.40134800	-3.13355000
H	0.93959000	0.84775500	-2.83421600
C	4.10146300	-3.03958700	-1.27309100
F	4.64204200	-1.95009600	-1.83962300
F	3.59487200	-3.81020700	-2.24535200
F	5.08258000	-3.72296700	-0.66456000
N	-3.21861000	-2.55568000	-0.15568000
N	1.93560900	3.83281600	1.70296900
O	1.79389200	-1.81715200	-0.90662100
O	3.47919800	-1.69614200	0.95292000
O	2.27024600	-3.85889100	0.49379500
P	-2.16890100	-0.49859600	0.79768500
P	0.92199200	2.20657900	-0.21297300
Pd	-0.16345400	-1.00276800	-0.13450200
S	2.76129700	-2.55975600	-0.01778000
H	0.45460400	0.76355700	-0.13351400

C	3.62877900	-1.52712700	-1.85831800
H	4.41219300	-0.86265400	-1.51387300
C	3.65432500	-1.97492500	-3.16946400
H	4.44369100	-1.64777500	-3.83754000
C	2.67750300	-2.85812100	-3.60984500
H	2.69095600	-3.23697800	-4.62590500
C	1.68712600	-3.26376000	-2.72972100
H	0.93434500	-3.96934000	-3.06590300
C	1.63141800	-2.79629800	-1.41285300
C	0.53217100	-3.32569200	-0.52944000
H	0.87304800	-3.49193400	0.49462900
H	0.17898000	-4.29002000	-0.89730800
C	-1.83369700	-2.92215800	1.12718800
C	-2.56211400	-2.07769900	1.95923600
H	-2.62192400	-1.01525400	1.75781600
C	-3.20431700	-2.63498900	3.05741300
H	-3.78202300	-2.00856500	3.72756000
C	-3.08765200	-3.99830600	3.28059400
H	-3.57020100	-4.47356700	4.12632200
C	-2.32683500	-4.75478800	2.39655000
H	-2.20794800	-5.82397800	2.54449800
C	-2.09941800	-2.27449300	-1.82364100
C	-3.42684700	-1.64335600	-1.39503200
H	-3.29205200	-0.63198500	-1.00519400
H	-3.94781500	-2.24441900	-0.64762200
H	-4.07121200	-1.57468100	-2.27658200
C	-2.32020200	-3.71162000	-2.29170500
H	-2.75132900	-4.33628000	-1.50588800
H	-1.39581500	-4.17814300	-2.63746600
H	-3.02140000	-3.70087600	-3.13207500
C	-1.46097500	-1.42264200	-2.92425500
H	-2.14154500	-1.39786500	-3.78076300
H	-0.50761700	-1.82841100	-3.26368900
H	-1.29911200	-0.39455300	-2.59233400
C	-3.82133500	3.47613100	-1.06115700
F	-4.59426600	2.49775500	-1.54230400
F	-3.17913200	4.04427500	-2.08457600
F	-4.61347100	4.39554600	-0.50115600
N	3.07875400	2.57873300	-0.27529800
N	-1.70813900	-4.23532700	1.33746200
O	-1.84756800	1.80693300	-0.62200300
O	-3.46119800	2.20531900	1.25101000
O	-1.81691100	3.99234900	0.61283100
P	2.10627000	0.30129700	0.80857500
P	-0.95379700	-2.24260100	-0.33509200
Pd	0.09368100	0.90861700	0.02403900
S	-2.60040300	2.80816400	0.21315000
H	-0.45542700	-0.79202700	-0.04220100

[H$_{py}$L2Pd-OTf]

C	1.11708900	-2.57253800	0.03281000
C	1.65325000	-2.33775100	-1.27842800
H	1.19053200	-1.70750500	-2.02405400
C	2.89295100	-3.01987400	-1.39441900
H	3.54096000	-3.01360700	-2.25763100
C	3.14905200	-3.67212600	-0.15684900
H	4.03206000	-4.24125000	0.09184500
C	2.06563200	-3.39662000	0.72561400
H	1.99958400	-3.73128800	1.74877700
C	2.98862800	0.36889100	0.06752700
C	4.19606800	-0.19268200	-0.45644800
H	4.58298300	-0.06546000	-1.45537200
C	4.79903900	-0.99242100	0.55755300
H	5.70502600	-1.56977700	0.44841700
C	3.97443800	-0.93669300	1.71446500
H	4.14359800	-1.45878800	2.64422200
C	2.86011800	-0.11353000	1.40985000
H	2.02601000	0.10794200	2.05971900
C	-1.61813700	-2.88490300	-0.44446600
C	-1.31737000	-4.11667400	-1.01402400
H	-0.32041200	-4.51879500	-0.89537600
C	-2.28962300	-4.82493200	-1.69694900
H	-2.05156000	-5.79115500	-2.12417800
C	-3.57322300	-4.30501700	-1.82681800
H	-4.35061100	-4.83592500	-2.35553600
C	-3.84091700	-3.07768900	-1.27297800
H	-4.79919600	-2.58202700	-1.33430400
C	-0.88417400	-2.29912000	2.26257200
C	0.16675800	-1.66928000	3.17054100
H	-0.05456100	-1.91940700	4.21125300
H	0.15847200	-0.58093700	3.08136300
H	1.17606900	-2.01979100	2.94898200
C	-0.92710700	-3.81103800	2.44201300
H	-1.09935400	-4.04735000	3.49583700
H	-0.00163700	-4.30332100	2.14582600
H	-1.74230600	-4.26327600	1.87423400
C	-2.25067000	-1.70877800	2.59689400
H	-3.05231900	-2.16467100	2.01258000
H	-2.28576900	-0.62990700	2.43218200
H	-2.47794800	-1.89854000	3.64929500
C	2.00092400	2.99393000	0.37700000
C	0.95272600	3.88825800	0.59159400

[H$_{py}$L2Pd-OTf]

C	1.14082400	-2.63867200	-0.07446200
C	1.42593900	-2.50283100	-1.47494900
H	0.84451300	-1.92795300	-2.17794400
C	2.59093400	-3.25666400	-1.77619600
H	3.05362600	-3.34500000	-2.74680700
C	3.05963100	-3.83959100	-0.56616500
H	3.94516600	-4.44536100	-0.45147900
C	2.17500400	-3.45765200	0.48162900
H	2.28447500	-3.73816000	1.51500600
C	3.22212100	0.35879100	-0.35112800
C	4.11242800	-0.21554100	-1.30969000
H	4.11997200	-0.02696800	-2.36945200
C	4.99947900	-1.10171500	-0.63356300
H	5.77701500	-1.68891200	-1.09727500
C	4.65993700	-1.09417200	0.74732400
H	5.13709000	-1.67068100	1.52455900
C	3.55713800	-0.21563300	0.91816300
H	3.05748100	-0.00388300	1.84981800
C	-1.68242400	-2.81507300	-0.16437200
C	-1.54827300	-4.09771600	-0.68371000
H	-0.60250400	-4.61043700	-0.59012200
C	-2.62223400	-4.71651000	-1.31181800
H	-2.50999200	-5.71855000	-1.70657400
C	-3.83956600	-4.05187000	-1.43028100
H	-4.69084200	-4.50555000	-1.91708400
C	-3.94245400	-2.77846400	-0.91484300
H	-4.83751500	-2.17565900	-0.96498200
C	-0.50722200	-2.36919600	2.49705400
C	0.66977700	-1.76378400	3.27856200
H	0.53467500	-1.97999300	4.34257100
H	0.70980800	-0.67957600	3.15832600
H	1.63085200	-2.17726000	2.97445600
C	-0.55319200	-3.89016100	2.68309500
H	-0.62040000	-4.11511200	3.75231200
H	0.33524800	-4.39029600	2.29878300
H	-1.42811200	-4.33248000	2.20380100
C	-1.84170900	-1.75169100	3.02138000
H	-2.69708200	-2.16517800	2.52992500
H	-1.82556700	-0.66759500	2.89711600
H	-1.90448800	-1.97149700	4.08924100
C	2.47752500	2.93401900	0.64640500
C	1.54760000	3.64347900	1.40885100

[H$_{py}$L2Pd-OTf]

C	1.12573700	-2.59096000	-0.09856700
C	1.34799700	-2.40995400	-1.50396900
H	0.74160600	-1.80029000	-2.15703200
C	2.48655600	-3.16762500	-1.88304200
H	2.90664200	-3.22552200	-2.87651300
C	3.00223900	-3.79446700	-0.71616600
H	3.88822200	-4.41043800	-0.66225900
C	2.17324500	-3.43701300	0.38376000
H	2.32877300	-3.74842400	1.40413200
C	3.17788300	0.32854600	-0.40367600
C	4.02918200	-0.23228400	-1.40302800
H	3.99961300	-0.02539000	-2.46063400
C	4.92896100	-1.13899600	-0.77474700
H	5.68210900	-1.72882100	-1.27698500
C	4.63547700	-1.15793200	0.61507300
H	5.13023100	-1.75942300	1.36366900
C	3.54801700	-0.27428100	0.84074200
H	3.07867800	-0.07719700	1.79269400
C	-1.67350400	-2.74964100	-0.10885900
C	-1.55688800	-4.03042300	-0.63186200
H	-0.61320300	-4.55175900	-0.54745800
C	-2.64178500	-4.63403600	-1.25151700
H	-2.54517800	-5.63700400	-1.65142400
C	-3.84952600	-3.95431600	-1.35648300
H	-4.71215900	-4.39506100	-1.83782100
C	-3.93095100	-2.68206100	-0.83770100
H	-4.82010800	-2.06785300	-0.88138300
C	-0.43637700	-2.38902300	2.51000900
C	0.75768100	-1.80503600	3.26934300
H	0.65692200	-2.05009000	4.33179700
H	0.79066400	-0.71673700	3.17519400
H	1.71748700	-2.20738300	2.92254400
C	-0.47906700	-3.90879700	2.65285200
H	-0.51289200	-4.16474800	3.71751700
H	0.39639800	-4.39943800	2.22586300
H	-1.37086500	-4.33567900	2.18874700
C	-1.77524700	-1.78743200	3.07788300
H	-2.61937900	-2.18900600	2.59443700
H	-1.74094100	-0.69932200	2.98017400
H	-1.79256100	-2.03382600	4.14247600
C	2.53230000	2.88341900	0.66013600
C	1.65527300	3.59486200	1.47768000

H   -0.03585400   3.65875200   0.20728500
C   1.19408800   5.04946900   1.30613500
H   0.39773600   5.76292600   1.48067000
C   2.46680700   5.26938300   1.80813800
H   2.70004200   6.15524100   2.38465900
C   3.44383900   4.31600100   1.56457100
H   4.45001600   4.45105000   1.95150800
C   2.18791700   1.96335400 -2.33800300
C   2.18847500   0.71096600 -3.20929400
H   2.43551800   0.97731600 -4.24053300
H   1.20277800   0.23910300 -3.21535300
H   2.91332400 -0.03294100 -2.87565500
C   3.54373800   2.65596200 -2.37324900
H   4.34115900   2.05228700 -1.94144500
H   3.52480100   3.60567100 -1.83731700
H   3.81774200   2.87299900 -3.41054900
C   1.11643100   2.92270800 -2.85061000
H   1.07451700   3.84076300 -2.26139800
H   0.12356800   2.46693100 -2.83340800
H   1.33898500   3.20698000 -3.88252100
Fe   2.94351700 -1.67515800   0.12501200
N   -2.87635500 -2.41403800 -0.61958500
N   3.23359600   3.20244000   0.86145400
O   -3.04382600   1.76979400   1.60879100
P   -0.46196600 -1.76102500   0.47964400
P   1.65713400   1.44434300 -0.58997200
Pd -0.38344500   0.39524000 -0.19896700
S   -3.43278300   1.36100900   0.24659100
C   -4.93568800   2.42164600 -0.12922700
O   -4.00745700 -0.01290400   0.13015600
O   -2.48931900   1.73216600 -0.84048200
F   -4.61981000   3.71818300 -0.08847800
F   -5.90597100   2.20001000   0.76189300
F   -5.41723100   2.14721300 -1.34460600
H   -3.11497600 -1.46840500 -0.26258600

H   0.49421100   3.40561300   1.33376700
C   1.99664500   4.64288100   2.26463900
H   1.29316300   5.20846000   2.86383900
C   3.36082200   4.89131500   2.34439800
H   3.75941300   5.65242200   3.00336700
C   4.21661700   4.12838500   1.55631600
H   5.28927400   4.28944400   1.59459800
C   1.94178600   2.40560300 -2.23058500
C   1.50710700   1.36173800 -3.27148400
H   1.43990100   1.84153000 -4.25302400
H   0.52488800   0.94872400 -3.03193800
H   2.21306200   0.53520200 -3.35623100
C   3.32058500   2.97531100 -2.58584100
H   4.09962100   2.21359300 -2.59645100
H   3.62717200   3.75512400 -1.88647100
H   3.27584600   3.42052600 -3.58361500
C   0.90989000   3.54595100 -2.22246300
H   1.17694700   4.33728700 -1.51946700
H   -0.08982000   3.18627100 -1.96983300
H   0.86415200   3.99238700 -3.22043600
Fe   3.05108300 -1.76751000 -0.39016900
N   -2.88336800 -2.20938400 -0.31472600
N   3.79360700   3.17465600   0.72221200
O   -3.53097400   2.58329800   0.95848600
P   -0.32759300 -1.79852200   0.66720600
P   1.84488400   1.58766200 -0.49752900
Pd -0.07248200   0.41795100   0.15078500
S   -4.01051600   1.61371100 -0.05469400
C   -5.85789200   2.02504900 -0.22066200
O   -4.05708700   0.18929600   0.41690500
O   -2.49055400   1.78798800 -1.43332400
F   -6.02565400   3.28588200 -0.64820100
F   -6.48819900   1.89708500   0.95751000
F   -6.45544300   1.20457000 -1.10168700
H   -3.02882200 -1.24003900   0.02277900

H   0.59412700   3.37436800   1.45044100
C   2.16486500   4.56994000   2.32460300
H   1.50295400   5.13914000   2.96831400
C   3.53426600   4.78968800   2.33972500
H   3.98132300   5.53189500   2.99079400
C   4.33293700   4.02368000   1.49908500
H   5.41061800   4.16312700   1.48766800
C   1.83752700   2.40573900 -2.17424800
C   1.34849200   1.37726800 -3.19727000
H   1.24154700   1.86364700 -4.17296600
H   0.37304800   0.97228800 -2.91432200
H   2.04320400   0.54425200 -3.31658500
C   3.19483200   2.97249200 -2.58472800
H   3.97011600   2.20771100 -2.64172200
H   3.53683600   3.74422700 -1.89333600
H   3.10452700   3.42957200 -3.57683200
C   0.81473900   3.54339500 -2.09554300
H   1.12350300   4.32488600 -1.39709600
H   -0.17062900   3.18073500 -1.79102700
H   0.71445100   4.00370300 -3.08409800
Fe   3.00206900 -1.75871200 -0.47720500
N   -2.86336200 -2.12854000 -0.24661000
N   3.85273700   3.09433300   0.67346500
O   -3.40836800   2.74584400   0.56068600
P   -0.30359800 -1.76616700   0.71210900
P   1.81871100   1.57193600 -0.46298400
Pd -0.06250600   0.43712900   0.24715800
S   -3.99766200   1.62327500 -0.19589700
C   -5.85184200   1.97792400 -0.14074600
O   -3.91955800   0.29836500   0.49635400
O   -3.69561600   1.57282500 -1.64228400
F   -6.12438000   3.14323900 -0.73606500
F   -6.29086700   2.04110400   1.12014900
F   -6.53961100   1.01824300 -0.77200000
H   -2.99187600 -1.15252600   0.09087400

[L2Pd-H(OTf)]

Pd -0.32120500 -0.22705000   0.79873700
C   1.67911600   2.43071300   1.28212800
C   2.72978400   3.28028200   0.95242600
N   1.42792800   2.05175000   2.54456000
C   3.57202500   3.72100300   1.96279900
H   2.87984400   3.60985000 -0.06576000
C   2.22973300   2.50565600   3.50548900
C   3.32056400   3.32880000   3.26518000
H   4.40452100   4.37366700   1.73080700
H   1.98992500   2.18653400   4.51509500
H   3.94985500   3.65472700   4.08302600
C   -0.79382200   3.20712500 -0.12361300
C   -1.85883300   2.78573400 -1.12956800
H   -1.46134000   2.73161200 -2.14318000
H   -2.29905700   1.81879300 -0.88070400
H   -2.66139500   3.52717800 -1.12914700
C   -1.42676100   3.46461400   1.23978600
H   -2.20026300   4.22898200   1.13801200
H   -1.89513600   2.56462600   1.64217600
H   -0.69904600   3.82437700   1.96897600
C   -0.06904100   4.45322300 -0.61946400
H   -0.79787100   5.25230600 -0.77411700
H   0.66354500   4.81871200   0.10127800
H   0.43572100   4.28429200 -1.57283800
C   0.47195800 -2.92963800   0.62724600
C   0.60539600 -4.27400000   0.33268700
N   -0.72553200 -2.38488000   0.94932100
C   -0.52369400 -5.07940500   0.40479000
H   1.56736900 -4.67712500   0.04339600
C   -1.81346400 -3.15500600   1.00226600
C   -1.74110700 -4.51613300   0.74820000
H   -0.45183400 -6.13771700   0.18628400
H   -2.75067800 -2.65435300   1.22432900
H   -2.63897800 -5.11674200   0.80174200
C   2.97624900 -1.97769600   1.95901100
C   3.83074800 -0.73564400   2.20044400
H   4.41230700 -0.44520000   1.32516300
H   3.21875900   0.11442200   2.50125400
H   4.53875400 -0.93941600   3.00723800
C   3.84565700 -3.15835000   1.55279100
H   4.57189300 -3.35965900   2.34453800
H   3.26092600 -4.06780200   1.41025600
H   4.40432300 -2.96165700   0.63687400
C   2.18679000 -2.29536400   3.22696000
H   1.60755800 -3.21526800   3.13316500
H   2.88121800 -2.42543600   4.05991100
H   1.50019500 -1.48633800   3.48877600
H   -1.77088100   0.38890700   0.78142800
P   0.42464300   1.77680400   0.09524700
P   1.69859800 -1.54974700   0.64285100
Fe   2.19654600 -0.06874900 -2.35015900
C   1.80399800 -2.05010000 -2.17652600
C   3.83233000 -1.16684200 -2.81420800
C   2.65154700 -1.79554400 -3.28943600
C   0.41937200   0.86444700 -2.58019300

[L2Pd-H(OTf)]

Pd -0.16053400 -0.08675400   0.51406500
C   1.96486300   2.50078200   1.34176000
C   3.02228000   3.39624000   1.17491200
N   1.57881200   2.07104000   2.55025900
C   3.70900800   3.83979800   2.30000200
H   3.30182900   3.75444300   0.19596700
C   2.23468800   2.51488000   3.62473300
C   3.30950000   3.39412500   3.55191500
H   4.53676500   4.53048800   2.19493300
H   1.88509900   2.14762500   4.58352000
H   3.81243000   3.71828000   4.45392500
C   -0.17156900   3.38374200 -0.55761300
C   -1.11392900   2.98125300 -1.70025300
H   -0.57429500   2.76896600 -2.62356100
H   -1.72485800   2.11481100 -1.44356000
H   -1.78974000   3.81773800 -1.89900400
C   -1.00020200   3.79214700   0.66940100
H   -1.64193400   4.63339100   0.39318100
H   -1.64388400   2.97932900   1.01029500
H   -0.37479000   4.11152200   1.50476800
C   0.70807800   4.55464500 -1.01643700
H   0.05704700   5.36286100 -1.36139100
H   1.32117300   4.95451900 -0.20905700
H   1.35879600   4.27900500 -1.84831600
C   0.24092600 -2.88777100   0.42555900
C   0.19388000 -4.24211200   0.13593800
N   -0.88667500 -2.14041800   0.51093100
C   -1.05242900 -4.83993200 -0.04003900
H   1.10516100 -4.81750100   0.05167800
C   -2.08420400 -2.70923500   0.34154900
C   -2.20126300 -4.06864900   0.07302300
H   -1.12152700 -5.89764900 -0.26229300
H   -2.95326400 -2.06646300   0.41321400
H   -3.18394100 -4.50232300 -0.05639300
C   2.52789900 -2.42504800   2.33817000
C   3.46789800 -1.33293000   2.87316200
H   4.28348000 -1.10941700   2.18517600
H   2.92775400 -0.40828300   3.08030800
H   3.91436700 -1.68080100   3.80915600
C   3.31000200 -3.71042600   2.04957700
H   3.78654300 -3.91050100   2.97440500
H   2.66199500 -4.51517700   1.70003700
H   4.09644500 -3.55524700   1.30969900
C   1.42710300 -2.68664700   3.37831300
H   0.76459700 -3.50155700   3.03816200
H   1.89827000 -2.96649600   4.32467800
H   0.81923000 -1.79709500   3.55858700
H   -1.47280500   0.66576200   0.17942600
P   0.89019000   1.86935800 -0.04840300
P   1.66314600 -1.71798500   0.78234500
Fe   3.00655500 -0.27805100 -2.03131200
C   2.41176400 -2.28296500 -1.96585100
C   4.60994300 -1.60194500 -2.05257300
C   3.53598400 -2.12669000 -2.82268300
C   1.43624600   0.91939300 -2.69876900

[L2Pd-H(OTf)]

Pd -0.12172900 -0.05348500   0.51545300
C   2.06346400   2.46813000   1.30183700
C   3.14609700   3.32414100   1.11018700
N   1.66291200   2.08288800   2.51757100
C   3.84571300   3.77480500   2.22219500
H   3.43538700   3.64886300   0.12084100
C   2.33100000   2.53477400   3.57737800
C   3.43202700   3.37621200   3.48315600
H   4.69549800   4.43712400   2.09955200
H   1.96878400   2.20524500   4.54667300
H   3.94471200   3.70874900   4.37799700
C   -0.04392500   3.36592000 -0.58888300
C   -0.98130000   2.97599100 -1.73153600
H   -0.43769000   2.73920400 -2.64775900
H   -1.61682000   2.12719700 -1.46964400
H   -1.63480800   3.82728900 -1.94605900
C   -0.86710000   3.79676700   0.62631700
H   -1.49307300   4.64810000   0.34177400
H   -1.52654800   2.99582200   0.96905500
H   -0.23863900   4.11003000   1.46289300
C   0.86468200   4.50690500 -1.04659600
H   0.23593700   5.32995100 -1.40030100
H   1.48211400   4.89568400 -0.23577600
H   1.51354900   4.21026900 -1.87403200
C   0.19776000 -2.83446200   0.42299700
C   0.12186300 -4.18263100   0.12051300
N   -0.90900100 -2.06138600   0.51083600
C   -1.13672600 -4.74688000 -0.06386300
H   1.02075600 -4.77898200   0.03326700
C   -2.11651900 -2.59807400   0.33350000
C   -2.26522000 -3.95021500   0.05355800
H   -1.23134400 -5.80173400 -0.29605800
H   -2.97168000 -1.93498800   0.40832700
H   -3.25887300 -4.35916200 -0.08182400
C   2.44040300 -2.41865700   2.36528200
C   3.37619000 -1.34513600   2.92610100
H   4.21313800 -1.12987400   2.25982700
H   2.84042600 -0.41448800   3.12167100
H   3.79393100 -1.70208700   3.87282200
C   3.20837900 -3.70721000   2.08503900
H   3.65560000 -4.06330000   3.01921200
H   2.55823400 -4.49960200   1.70983800
H   4.01712500 -3.55446900   1.36751200
C   1.31047100 -2.66747900   3.36814300
H   0.64465000 -3.47219700   3.05021600
H   1.75038900 -2.95752800   4.32730200
H   0.71038200 -1.76863500   3.53427900
H   -1.39910800   0.74240200   0.15191500
P   0.96933200   1.84299700 -0.06392100
P   1.63006100 -1.71798500   0.80310900
Fe   3.01654600 -0.34947000 -2.00541600
C   2.43948700 -2.32426300 -1.90771600
C   4.62861600 -1.61534600 -1.96043300
C   3.58199600 -2.17744600 -2.73978600
C   1.44144700   0.78597900 -2.67077000

Top section (three columns):

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C   2.39830500   1.58075200  -3.50662300     C   3.65486000   1.39797400  -3.07191600     C   3.64696700   1.24154000  -3.12968500
C   1.16955300   0.92189000  -3.78410100     C   2.47218500   0.88233700  -3.66999100     C   2.44711600   0.70498100  -3.66926800
H   0.82396600  -2.50232800  -2.20903400     H   1.44092400  -2.64893800  -2.25788600     H   1.47860300  -2.70986200  -2.21226700
H   4.65823500  -0.82657500  -3.41966600     H   5.59495800  -1.35727700  -2.41787500     H   5.61867000  -1.36348700  -2.31074100
H   2.41996500  -2.02222500  -4.31936900     H   3.55935600  -2.35273500  -3.87707400     H   3.63380900  -2.43053200  -3.78837100
H  -0.55215200   0.40998400  -2.45112400     H   0.42342100   0.58087900  -2.84204500     H   0.42254100   0.44376200  -2.76719900
H   3.20439400   1.74284200  -4.20558500     H   4.62408700   1.47477300  -3.53909400     H   4.60397100   1.29089500  -3.62788500
H   0.87456800   0.49774900  -4.73135300     H   2.38020700   0.50047600  -4.67451100     H   2.32599500   0.27588100  -4.65285100
C   3.72065100  -1.01689900  -1.40415700     C   4.15191600  -1.42187100  -0.71792200     C   4.13619400  -1.40181800  -0.64440600
C   2.47196900  -1.58985600  -0.99733900     C   2.79106800  -1.86615100  -0.65123700     C   2.78163900  -1.86431700  -0.59879000
C   2.41109500   1.94048400  -2.13127000     C   3.35134900   1.76214900  -1.73105000     C   3.38521600   1.66452900  -1.79826800
C   1.17088800   1.52176600  -1.54673600     C   1.96392900   1.49412900  -1.49352600     C   2.00657000   1.41047900  -1.50885800
H   4.45931800  -0.56939300  -0.75826400     H   4.73657300  -1.02948900   0.09673600     H   4.69382800  -0.97145800   0.17190500
H   3.22630300   2.43414700  -1.62937200     H   4.05677100   2.16456100  -1.02526400     H   4.11504600   2.09223800  -1.13071900
O  -4.64249000  -1.48564400   0.95941900     O  -5.01414000  -1.12680400   0.40935700     O  -5.10392500  -1.05177700   0.43467900
S  -4.88611400  -0.86156200  -0.36476600     S  -5.87390200  -0.52922400  -0.65168400     S  -5.96463200  -0.47797000  -0.63122700
C  -5.32267700   0.90995300   0.09923800     C  -6.75038100   0.88255500   0.27055900     C  -6.85700900   0.92426700   0.26628100
O  -6.10784400  -1.31917300  -1.06358800     O  -7.00240200  -1.38453600  -1.10489300     O  -7.07591200  -1.35019200  -1.07814500
O  -3.68795400  -0.70043300  -1.22002300     O  -5.13874300   0.18266300  -1.73108800     O  -5.23654900   0.22716900  -1.71267400
F  -4.37318400   1.47568900   0.85609200     F  -5.86255100   1.75765000   0.77588400     F  -5.98508900   1.81574800   0.75658300
F  -6.46966400   0.95363200   0.79119900     F  -7.48798600   0.41100100   1.29149400     F  -7.58378100   0.45627000   1.28981100
F  -5.47724400   1.67039500  -0.99396600     F  -7.57181100   1.56076900  -0.55055100     F  -7.68570600   1.57483500  -0.56140700
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[HₚL2Pd-OTf]   [HₚL2Pd-OTf]   [HₚL2Pd-OTf]

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C  -2.23120200  -0.02555000  -1.46331600     C  -2.52411500  -0.29045600  -1.26166100     C  -2.47160900   0.33599400   1.26790900
C  -3.44282900   0.64497200  -1.84752700     C  -3.92082700   0.03861500  -1.25316100     C  -3.87726300   0.05402900   1.28815200
H  -4.45043700   0.35408900  -1.60119200     H  -4.70064500  -0.48849200  -0.73116100     H  -4.65266300   0.61605600   0.79371900
C  -3.10114400   1.80110400  -2.60270900     C  -4.11469000   1.21439300  -2.02938400     C  -4.08869600  -1.13203200   2.04288900
H  -3.80094000   2.52109300  -2.99881900     H  -5.05705700   1.71505000  -2.19009100     H  -5.04335100  -1.60771300   2.21523800
C  -1.68410700   1.86402500  -2.70434200     C  -2.84802800   1.63072700  -2.52598700     C  -2.82477000  -1.60151200   2.49428200
H  -1.10985300   2.63914600  -3.18926900     H  -2.65559100   2.50242600  -3.13168900     H  -2.64531400  -2.49565500   3.07284300
C  -1.15422500   0.74331600  -2.01817300     C  -1.87338500   0.71376000  -2.05397300     C  -1.83325600  -0.70677800   2.01686200
H  -0.11053800   0.49289600  -1.88374700     H  -0.81251300   0.76361200  -2.23717200     H  -0.76692000  -0.79710800   2.16066700
C  -1.09639600   2.45963600   0.76383300     C  -1.47251700   2.40751800   0.89433700     C  -1.56777800  -2.32768400  -0.89944900
C  -2.23649200   1.74044800   1.26277900     C  -2.41304500   1.57548400   1.59436400     C  -2.47298500  -1.43504200  -1.56685600
H  -2.19872100   0.82417600   1.83414900     H  -2.17650200   0.68641500   2.15523400     H  -2.19760100  -0.54419900  -2.10933900
C  -3.39957900   2.43614100   0.84445500     C  -3.70579200   2.12161600   1.39463100     C  -3.78835500  -1.92096200  -1.36181400
H  -4.41671300   2.13487500   1.04211600     H  -4.62619900   1.71289000   1.78053500     H  -4.69289000  -1.46011600  -1.72955100
C  -2.99384200   3.57346000   0.09107700     C  -3.58141200   3.27681300   0.57168200     C  -3.71071800  -3.09721100  -0.56571000
H  -3.65234600   4.28448300  -0.38333600     H  -4.39229600   3.89756000   0.22423600     H  -4.54772800  -3.68580700  -0.22016200
C  -1.57650800   3.59616400   0.02966300     C  -2.21059800   3.46048600   0.25787900     C  -2.34724300  -3.35403900  -0.27293600
H  -0.96020200   4.32022700  -0.47878000     H  -1.78988000   4.24210700  -0.35124700     H  -1.95684700  -4.16806200   0.31612200
C  -3.05892200  -1.59430800   0.90231000     C  -2.58910300  -2.26019200   0.93746100     C  -2.49375900   2.32689200  -0.89775100
H  -4.39380500  -1.20930200   0.80050200     H  -3.94687600  -2.58770200   0.88773900     H  -3.83592100   2.69932000  -0.81688900
H  -4.79888300  -0.85438700  -0.13563300     H  -4.50470700  -2.51737000  -0.03288400     H  -4.37981000   2.63012600   0.11413300
C  -5.20748400  -1.28403300   1.92047900     C  -4.58625600  -3.01975300   2.04415800     C  -4.47671000   3.17534900  -1.95291100
H  -6.24427200  -0.97471700   1.86374400     H  -5.63836400  -3.27743900   2.02101500     H  -5.51965500   3.46985700  -1.90813800
C  -4.67662400  -1.76742300   3.10397900     C  -3.85584200  -3.12016700   3.22019300     C  -3.76166600   3.27303500  -3.13627000
H  -5.27504300  -1.84137500   4.00272500     H  -4.31155100  -3.45502800   4.14328900     H  -4.21950000   3.64209600  -4.04654200
C  -3.34751900  -2.16229300   3.10944700     C  -2.50950000  -2.77779800   3.18320500     C  -2.42922800   2.88337100  -3.12701300
H  -2.89589300  -2.56399300   4.01178100     H  -1.89881500  -2.84241600   4.07772800     H  -1.83019400   2.94441800  -4.03123000
C  -2.28532700  -2.95274300  -1.59786000     C  -1.70360100  -3.08697700  -1.83597200     C  -1.52878400   3.07976600   1.85164600
C  -1.36229500  -2.87858200  -2.81044200     C  -0.83275000  -2.66725600  -3.03151200     C  -0.69778900   2.57463300   3.03720300
H  -1.52957700  -3.74430100  -3.45648800     H  -0.81972300  -3.47875400  -3.76553800     H  -0.62078500   3.37358300   3.78237300
H  -0.31071700  -2.87722200  -2.51078800     H   0.19692700  -2.46627600  -2.72869400     H   0.31430200   2.29846400   2.72841100
H  -1.54407600  -1.98194200  -3.40669500     H  -1.22381400  -1.77741800  -3.52958500     H  -1.15633100   1.71050400   3.52480400
C  -3.73875900  -2.90417200  -2.04398700     C  -3.12766000  -3.36276000  -2.33091200     C  -2.92841000   3.43952500   2.33878900
H  -3.93612500  -3.72536100  -2.73892300     H  -3.08282400  -4.09125500  -3.14691000     H  -2.83934300   4.14855000   3.16927900
H  -3.98011900  -1.97570600  -2.56491700     H  -3.61163900  -2.46539400  -2.72032300     H  -3.47759700   2.57038600   2.70851900
H  -4.43000000  -3.01949100  -1.20788800     H  -3.76074400  -3.79311400  -1.55512900     H  -3.52217200   3.92821300   1.56489300
C  -2.01434000  -4.23319100  -0.81586500     C  -1.11619900  -4.35484100  -1.19815900     C  -0.85027400   4.29666400   1.23199500
H  -2.65001800  -4.31338800   0.06875200     H  -1.71058500  -4.69873100  -0.34881000     H  -1.41755300   4.69361100   0.38613000
H  -0.97395000  -4.28365900  -0.48562500     H  -0.09258100  -4.19200200  -0.85359600     H   0.15863800   4.05781200   0.88397000
H  -2.21267800  -5.10390100  -1.44635400     H  -1.09919800  -5.15920200  -1.94002700     H  -0.77184200   5.08961900   1.98326900
C   1.58413100   2.42704300  -0.48076100     C   1.04242600   2.91467700  -0.61817000     C   0.92508700  -2.97750500   0.57061900
C   2.32940900   1.50930100  -1.20983000     C   1.82060700   2.18669200  -1.51406100     C   1.75854900  -2.31683700   1.46629100
H   2.28525100   0.44788000  -0.98145400     H   1.96085700   1.12105300  -1.38437400     H   1.95270800  -1.25542200   1.35981100
C   3.11681800   1.98891100  -2.24576800     C   2.40876000   2.86945800  -2.57449800     C   2.32989100  -3.05742300   2.49393700
H   3.71355900   1.30560800  -2.83735200     H   3.02349200   2.33825700  -3.29028200     H   2.98791600  -2.57938600   3.21058500
C   3.11907600   3.34844400  -2.50427800     C   2.19348400   4.23503200  -2.69320800     C   2.04286100  -4.41016100   2.58135800
H   3.71611000   3.76562200  -3.30482700     H   2.63228100   4.80449000  -3.50231200     H   2.46665900  -5.02527200   3.36629800
C   2.33775900   4.18269400  -1.71473800     C   1.39708100   4.87199900  -1.74441800     C   1.19398700  -4.97543100   1.63538000
H   2.32090200   5.25304300  -1.89290400     H   1.20841600   5.93802300  -1.80741600     H   0.94833100  -6.03234600   1.67543700
C   1.36403700   2.18226300   2.52713500     C   1.18914000   2.50296400   2.40974100     C   1.05872900  -2.48796500  -2.42329300
C   0.54514100   1.45211400   3.58944000     C   0.65788800   1.57526600   3.51383500     C   0.55711600  -1.51888900  -3.49740100
H   1.01903300   1.59343600   4.56257500     H   1.21733700   1.77644900   4.43123600     H   1.10064900  -1.72120400  -4.42517600
H   0.49278000   0.37805700   3.39625400     H   0.79324900   0.52150700   3.26234500     H   0.73573300  -0.47616600  -3.22382600
H  -0.47180000   1.84114900   3.65814300     H  -0.39762300   1.75287900   3.72415400     H  -0.50716100  -1.65059000  -3.70226600
C   1.37578700   3.68487800   2.77789700     C   0.93832900   3.97184900   2.77182000     C   0.74144000  -3.93148000  -2.81090100
H   0.36677200   4.09906000   2.81193900     H  -0.12136400   4.17317500   2.93896800     H  -0.32817300  -4.08377500  -2.97250700
H   1.93994500   4.22044300   2.01326000     H   1.30188300   4.65149500   2.00043200     H   1.08208300  -4.64231100  -2.05607300
H   1.84852200   3.88246200   3.74264500     H   1.47207200   4.19663600   3.69980600     H   1.25739200  -4.16050400  -3.74896400
C   2.78047600   1.61900600   2.45415400     C   2.68544600   2.24183500   2.17423400     C   2.56000000  -2.29610100  -2.19660900
H   3.38826600   2.14876300   1.71874400     H   3.10693000   2.92299700   1.43326400     H   2.95766900  -3.00953800  -1.47164600
H   2.78502300   0.55584700   2.20408100     H   2.87719900   1.21630000   1.85233400     H   2.79747600  -1.28529600  -1.85637400
H   3.26074000   1.73571900   3.42745700     H   3.21659000   2.40281200   3.11587700     H   3.07783600  -2.46080600  -3.14597800
Fe -2.27226200   1.87053300  -0.75364800     Fe -2.83529600   1.60276100  -0.43673900     Fe -2.86941500  -1.50581600   0.43809700
N  -2.54748000  -2.07262500   2.04771000     N  -1.88912900  -2.35771400   2.07758200     N  -1.80723700   2.42106200  -2.04312400
N   1.57879200   3.74532900  -0.71049100     N   0.82982300   4.23202300  -0.71996400     N   0.64241800  -4.28091600   0.64212200
O   2.50755500  -1.58337900   0.75518600     O   2.83025500  -0.99175900   0.31033000     O   2.84805800   0.91625300  -0.32429900
P  -1.80424000  -1.50322500  -0.46560600     P  -1.55844900  -1.68009000  -0.52609200     P  -1.47179600   1.68975600   0.53341700
P   0.55853100   1.82266600   0.89365500     P   0.28712500   2.05323000   0.81865100     P   0.19818000  -2.03529100  -0.82241100
```

Pd	0.33752400	-1.53546800	0.17196500	Pd	0.61528400	-1.23009900	-0.03291500	Pd	0.66070400	1.18351700	0.02275200
S	3.48169400	-2.16919000	-0.23360400	S	3.87096400	-1.83900800	-0.38292000	S	3.88656800	1.73432200	0.39805500
C	5.06458800	-1.33149000	0.33299500	C	5.45372700	-1.19129100	0.44069400	C	5.46007700	1.10960200	-0.43520600
O	3.30763500	-1.68121000	-1.61670100	O	4.06142900	-1.52066700	-1.81782900	O	4.06584000	1.37093600	1.81780800
O	3.74514600	-3.60621600	-0.05813700	O	3.84294600	-3.27428400	-0.02040600	O	3.86124700	3.17506100	0.08213300
F	5.30424800	-1.57785400	1.62290700	F	5.41549500	-1.37587100	1.76822200	F	5.42819700	1.33976500	-1.75016100
F	4.97870500	-0.00680500	0.16907600	F	5.61703100	0.11982100	0.20473000	F	5.61318600	-0.20411100	-0.24317300
F	6.10615600	-1.77059700	-0.37740100	F	6.52591400	-1.83780100	-0.04094100	F	6.52748100	1.73233500	0.07314400
H	0.44844100	0.36428300	0.71018100	H	0.40663500	0.58475400	0.54091300	H	0.36522900	-0.55042200	-0.49405400

Computational part on the inversion barrier

Table SI-6 M06L/TZVP energetic data [CCSD(T)[18]/TZVP//M06L/TZVP references are included for comparison]
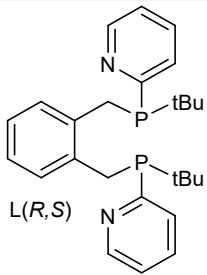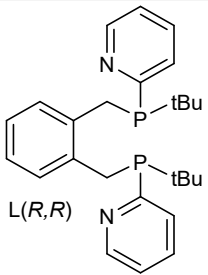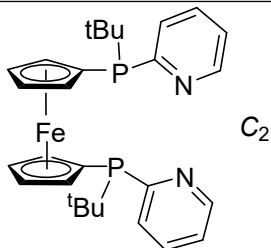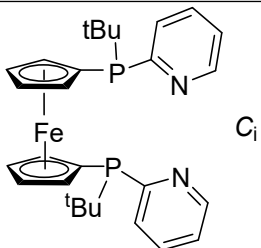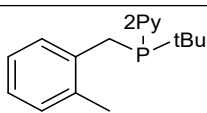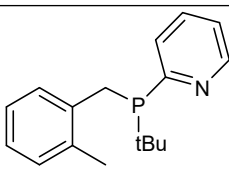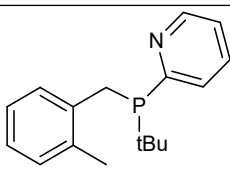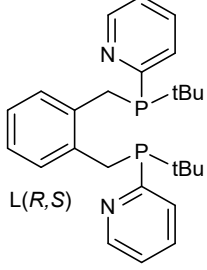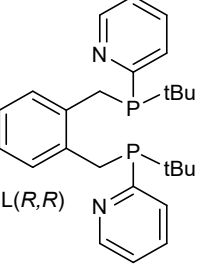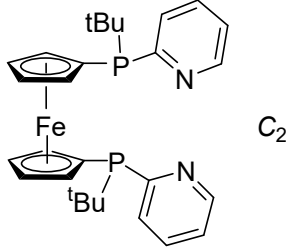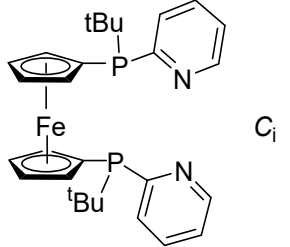
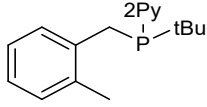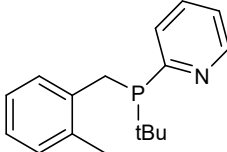|	M06L/TZVP		M06L/TZVP
L(*R,S*)	HF=-1803.6573788 ZPE=0.542494 NImag=0 Htot=-1803.082778 Gtot= -1803.177854	L(*R,R*)	HF=-1803.6561497 ZPE=0.542628 NImag=0 Htot=-1803.081430 Gtot= -1803.175339
C_2	HF=-3143.6098961 ZPE=0.553505 NImag=0 Htot=-3143.022075 Gtot=-3143.121123	C_i	HF=-3143.6077094 ZPE=0.553248 NImag=0 Htot=-3143.020881 Gtot= -3143.118802
	HF=-1057.2946579 ZPE=0.349035 NImag=0 Htot=-1056.925321 Gtot= -1056.993599		HF=-1057.2483897 ZPE=0.348016 NImag=1 (-251.3273) Htot=-1056.880574 Gtot= -1056.947162
	HF=-1057.245987 ZPE=0.347960 NImag=1 (-257.4881) Htot=-1056.878207 Gtot= -1056.944729		

Table SI-7 M06L/TZVP optimized Cartesian Coordinates

L(R,S)	L(R,R)
H,0,1.9205995679,0.024492888,-3.4618293659	H,0,1.8246848665,-3.0989750205,-1.6510175388
C,0,0.9780514072,0.5333680337,-3.2925337942	H,0,-1.8246848665,-3.0989750205,1.6510175388
C,0,-1.4052916757,1.8244772358,-2.8270664242	C,0,1.0219080184,-3.1051643093,-0.9212167197
C,0,0.4053510619,0.4524044038,-2.02223229	C,0,-1.0219080184,-3.1051643093,0.9212167197
C,0,0.3749871218,1.242274009,-4.3171910937	C,0,0.5274281622,-1.881777183,-0.4644579548
C,0,-0.8271669034,1.8928755274,-4.082774655	C,0,-0.5274281622,-1.881777183,0.4644579548
C,0,-0.8076568132,1.1193614436,-1.7820558188	C,0,0.515304567,-4.3092236717,-0.4653546781
H,0,0.8403996585,1.2854682537,-5.2943494883	C,0,-0.515304567,-4.3092236717,0.4653546781
H,0,-1.313805536,2.4500230772,-4.8738648188	H,0,0.9211573095,-5.24323254,-0.8335847179
H,0,-2.3498720937,2.3255506586,-2.6417039308	H,0,-0.9211573095,-5.24323254,0.8335847179
C,0,1.1179832302,-0.3186344547,-0.9546011864	C,0,1.1119926189,-0.6159040021,-1.0020205989
H,0,1.8628630992,-0.9795439743,-1.3981580577	C,0,-1.1119926189,-0.6159040021,1.0020205989
H,0,0.4111287372,-0.9224947553,-0.3826013821	H,0,2.1909552969,-0.7322696112,-1.1281856633
C,0,-1.4662444415,1.1174004085,-0.4302317774	H,0,-2.1909552969,-0.7322696112,1.1281856633
H,0,-0.8955356156,0.5504645751,0.3034271929	H,0,0.9606991035,0.2192988898,-0.3209290539
H,0,-1.535967603,2.1426817824,-0.0548244501	H,0,-0.9606991035,0.2192988898,0.3209290539
P,0,1.9830573195,0.7914565467,0.2697891243	P,0,0.4608049263,-0.1533010591,-2.7128874888
P,0,-3.2159117206,0.4709692465,-0.4608233157	P,0,-0.4608049263,-0.1533010591,2.7128874888
C,0,3.6653799658,0.90101675,-0.5162897514	C,0,1.1192418136,1.6170870764,-2.8831157725
C,0,6.1499517152,1.1253726336,-1.6392265541	C,0,-1.1192418136,1.6170870764,2.8831157725
N,0,4.0068299699,0.0579533018,-1.4994219344	C,0,0.4154183299,2.2388286515,-4.0881416875
C,0,4.5360724639,1.8959734884,-0.0656326986	C,0,-0.4154183299,2.2388286515,4.0881416875
C,0,5.7969807513,2.0011070706,-0.6244245904	H,0,0.5012562532,1.607181962,-4.9748777191
C,0,5.2175881138,0.1819908692,-2.0409580401	H,0,-0.5012562532,1.607181962,4.9748777191
H,0,6.4890136425,2.7617804201,-0.2836011796	H,0,0.8702261053,3.2042601742,-4.3258734537
H,0,5.4523828112,-0.5155959066,-2.8404199466	H,0,-0.8702261053,3.2042601742,4.3258734537
H,0,7.1204319609,1.175280014,-2.1155639816	H,0,-0.6413330464,2.4065115857,-3.8845842558
C,0,2.3319885994,-0.4555216772,1.6733679588	H,0,0.6413330464,2.4065115857,3.8845842558
C,0,2.8397748223,-1.7981199898,1.1664349562	C,0,0.9549662574,2.5144118762,-1.6614366563
H,0,2.0977550087,-2.3091310922,0.5519974769	C,0,-0.9549662574,2.5144118762,1.6614366563
H,0,3.070835533,-2.4542886813,2.0111160815	H,0,1.3421811044,3.5113782454,-1.8926521567
H,0,3.7464018366,-1.6929085844,0.5687524477	H,0,-1.3421811044,3.5113782454,1.8926521567
C,0,1.0054662284,-0.6358606382,2.4107709851	H,0,1.5183959363,2.151617862,-0.7997089445
H,0,0.6593340575,0.3055991875,2.8414755732	H,0,-1.5183959363,2.151617862,0.7997089445
H,0,1.1245380304,-1.351408482,3.2296118186	H,0,-0.089651255,2.6162382093,-1.3755964636
H,0,0.2129284355,-1.0116347603,1.7578494352	H,0,0.089651255,2.6162382093,1.3755964636
C,0,3.3559793831,0.1611102899,2.6200931639	C,0,2.6098043864,1.4637664105,-3.1955332908
H,0,4.3388577215,0.2516364602,2.1550222124	C,0,-2.6098043864,1.4637664105,3.1955332908
H,0,3.4714032405,-0.4670507107,3.5074899406	H,0,2.7824187954,0.8347470855,-4.0705813557
H,0,3.0493853928,1.1539559893,2.9565206634	H,0,-2.7824187954,0.8347470855,4.0705813557
H,0,4.2121837842,2.5769443923,0.7129892229	H,0,3.1612305865,1.033811065,-2.3560326542
C,0,-3.768394325,0.8601349174,1.3262536006	H,0,-3.1612305865,1.033811065,2.3560326542
C,0,-4.1130298169,2.3479275991,1.3554139383	H,0,3.047057109,2.4448621818,-3.3983678714
H,0,-3.2471005468,2.9746901458,1.1347423464	H,0,-3.047057109,2.4448621818,3.3983678714
H,0,-4.4705415302,2.6307466924,2.3492008696	C,0,1.340082133,0.0068748851,2.2912086688
H,0,-4.8958985421,2.5937329091,0.6364166036	C,0,-1.340082133,0.0068748851,-2.2912086688
C,0,-2.7057833822,0.5506899423,2.3721450565	C,0,3.9861220748,0.0933711316,1.6017028405
H,0,-1.8307724355,1.193260677,2.2676580617	C,0,-3.9861220748,0.0933711316,-1.6017028405
H,0,-2.3642619029,-0.4841503446,2.3170545385	C,0,2.0778621354,-1.1809220635,2.2468439069
H,0,-3.1104804024,0.715883616,3.3750967846	C,0,-2.0778621354,-1.1809220635,-2.2468439069
C,0,-5.0288834307,0.0490594794,1.6108331293	N,0,1.9027265536,1.1975035183,2.0449840726
H,0,-5.7915873183,0.2022949215,0.8441244066	N,0,-1.9027265536,1.1975035183,-2.0449840726
H,0,-5.4591722043,0.3509386467,2.5692856521	C,0,3.1946669897,1.2251453259,1.7183286084
H,0,-4.8207032046,-1.0203384717,1.6690551617	C,0,-3.1946669897,1.2251453259,-1.7183286084
C,0,-2.8977220935,-1.3544349166,-0.3122939164	C,0,3.4093592003,-1.1374857558,1.8766412836

C,0,-2.4903417824,-4.0536615392,-0.1040805897	C,0,-3.4093592003,-1.1374857558,-1.8766412836
C,0,-3.9115173081,-2.2342539936,-0.6966142293	H,0,1.5969357926,-2.1229292472,2.4845636409
N,0,-1.7201499836,-1.7980342809,0.1469938288	H,0,-1.5969357926,-2.1229292472,-2.4845636409
C,0,-1.5315931082,-3.1137988971,0.2377066602	H,0,3.6138073387,2.2106559278,1.5333263892
C,0,-3.7097502639,-3.5981627552,-0.5804152742	H,0,-3.6138073387,2.2106559278,-1.5333263892
H,0,-4.8427768424,-1.8386700858,-1.0847980923	H,0,3.9903402879,-2.0496892866,1.8115906442
H,0,-0.5576485463,-3.4276201143,0.6062151076	H,0,-3.9903402879,-2.0496892866,-1.8115906442
H,0,-4.4866392842,-4.2960509652,-0.8683181874	H,0,5.0262098316,0.1783593422,1.3147351186
H,0,-2.2820163141,-5.110978432,-0.0060031846	H,0,-5.0262098316,0.1783593422,-1.3147351186

tBu Fe C_2	tBu Fe C_i

C,0,-1.1397492344,0.6402823882,-1.6621733353	Fe,0,0.,0.,0.
C,0,1.1397492344,0.6402823882,1.6621733353	H,0,-2.3345550912,1.4220559549,-0.5115059531
C,0,-1.3482111057,-0.6504357107,-1.0722326378	H,0,2.3345550912,-1.4220559549,0.5115059531
C,0,1.3482111057,-0.6504357107,1.0722326378	C,0,-1.9040316419,0.4321727759,-0.5424745394
H,0,-1.135259528,-1.5865429274,-1.5616911553	C,0,1.9040316419,-0.4321727759,0.5424745394
H,0,1.135259528,-1.5865429274,1.5616911553	C,0,-1.9066558172,-0.5187562176,0.5103319823
C,0,-1.8147285767,-0.4648574002,0.2576835606	C,0,1.9066558172,0.5187562176,-0.5103319823
C,0,1.8147285767,-0.4648574002,-0.2576835606	H,0,-2.347620378,-0.3821804295,1.4853884162
H,0,-2.0244959189,-1.2470817027,0.971796821	H,0,2.347620378,0.3821804295,-1.4853884162
H,0,2.0244959189,-1.2470817027,-0.971796821	C,0,-1.1786745713,-1.6608521159,0.0697337679
C,0,-1.9064155937,0.9344447569,0.5056441591	C,0,1.1786745713,1.6608521159,-0.0697337679
C,0,1.9064155937,0.9344447569,-0.5056441591	H,0,-0.960011249,-2.5360354505,0.6635737057
H,0,-2.1900720334,1.396492371,1.4392443235	H,0,0.960011249,2.5360354505,-0.6635737057
H,0,2.1900720334,1.396492371,-1.4392443235	C,0,-0.7315569707,-1.4203473389,-1.2573915338
C,0,-1.489771436,1.6166763309,-0.6680172431	C,0,0.7315569707,1.4203473389,1.2573915338
C,0,1.489771436,1.6166763309,0.6680172431	H,0,-0.1204845099,-2.0668534832,-1.8651773221
H,0,-1.407625433,2.6860972464,-0.7912834451	H,0,0.1204845099,2.0668534832,1.8651773221
H,0,1.407625433,2.6860972464,0.7912834452	C,0,-1.1769969924,-0.1154493257,-1.6532745409
C,0,0.7305792757,-0.2728258202,-3.6432869031	C,0,1.1769969924,0.1154493257,1.6532745409
C,0,-0.7305792757,-0.2728258202,3.6432869031	C,0,0.7362628045,0.2848339355,-3.7831632134
C,0,1.9938999389,0.0785053189,-4.1215582447	C,0,-0.7362628045,-0.2848339355,3.7831632134
C,0,-1.9938999389,0.0785053189,4.1215582447	C,0,3.2024690822,-0.4434998764,-4.7187770062
H,0,2.2409753034,1.1260509653,-4.2477779074	C,0,-3.2024690822,0.4434998764,4.7187770062
H,0,-2.2409753034,1.1260509653,4.2477779074	N,0,1.0955237038,-1.0059165371,-3.7161863865
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C,0,2.5441056558,-2.2353488213,-4.2386775503	C,0,-2.8288489659,-0.8873849989,4.7995278545
C,0,-2.5441056557,-2.2353488213,4.2386775503	C,0,2.3005733809,-1.3441009691,-4.1706138577
C,0,1.2666085115,-2.498193596,-3.7658775214	C,0,-2.3005733809,1.3441009691,4.1706138577
C,0,-1.2666085115,-2.498193596,3.7658775214	H,0,1.2533913622,2.2881429527,-4.3535070197
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H,0,-0.9396195619,-3.5233078164,3.613304304	H,0,3.4993146012,1.6271157627,-5.2200879652
N,0,0.3730625238,-1.5548341577,-3.4748550233	H,0,-3.4993146012,-1.6271157627,5.2200879652
N,0,-0.3730625238,-1.5548341577,3.4748550233	H,0,2.5573389791,-2.3972156229,-4.0933696319
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H,0,3.397035343,-0.68897037,4.9467768053	C,0,-3.4945245853,0.5354466078,-4.0481272638
H,0,-1.9640386137,-1.3956896375,-4.1854221254	C,0,3.4945245853,-0.5354466078,4.0481272638
H,0,1.9640386137,-1.3956896375,4.1854221254	H,0,-3.5636973167,1.6231256597,-4.1044956366
H,0,-3.1244843734,-0.49140882,-3.2170429909	H,0,3.5636973167,-1.6231256597,4.1044956366
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2Py — P — tBu

TS1-N-Tbu

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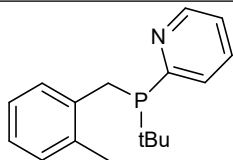
TS2-N-CH2.out

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C,0,1.4921856421,-1.7237181883,4.6915023291
C,0,2.7688116363,-2.0991026719,4.3032735151
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