Supporting Information

Development of highly efficient and selective palladium catalysts for telomerization of 1,3-butadiene with alcohols

Edson Leonardo Scarpa de Souza,[a‡] Sebastian Ahrens,[a‡] Anke Spannenberg,[a] Helfried Neumann,[a] Kathrin Junge,[a] Carlos Roque Duarte Correia,[b] Ralf Jackstell,[a*] and Matthias Beller[a*]

Abstract: A new class of ligands, alkyl (benzo)furylphosphines, allow efficient palladium-catalysed telomerization of 1,3-butadiene with methanol. The synthesis of industrially relevant 1 methoxy-2,7-octadiene (1-MODE) proceeds in the presence of these stable phosphine ligands in quantitative yield and excellent catalyst productivity (TON = 95.000), even at room temperature.

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1. General Information

All commercial reagents were obtained from the following chemical companies: Aldrich, Fisher Scientific, BLDpharm, TCI, ABCR and Strem. Unless otherwise noted, the commercial reagents were used without purification. The reactions with air- and moisture-sensitive reagents were carried out under argon atmosphere using standard Schlenk technique or in a M. Braun glovebox. Anhydrous and oxygen-free solvents (THF, DCM, diethyl ether, toluene, benzene, *n*-pentane, *n*-hexane and *n*-heptane) were received from an Innovative Technology PS-MD-6 solvent purification system or they were prepared by freeze-pump-thaw technique. All anhydrous solvent were stored over 3 Å molecular sieves under argon atmosphere.

NMR spectra were recorded on Bruker Avance 300 (300 MHz) or 400 (400 MHz) NMR spectrometers. The chemical shifts (δ) are reported in parts per million (ppm) and coupling constants (J) in hertz (Hz). All chemical shifts (δ) are given relative to solvent: references for THF-d_8 were 1.72 and 3.58 ppm (^{1}H), 67.21, and 25.31 ppm (^{13}C), for $CDCl_3$ 7.26 ppm (^{1}H) and 77.16 ppm (^{13}C) and for CD_2Cl_2 5.32 ppm (^{1}H) and 53.84 ppm (^{13}C). Multiplets of NMR were assigned as s (singlet), br s (broad singlet) d (doublet), t (triplet), q (quartet), ps-qui (pseudo-quintet), ps-h (pseudo-hextet), hept (heptet), ps-n (pseudo-nonet), dd (doublet of doublet), dt (doublet of triplet), dq (doublet of quartet), dh (doublet of heptet), ddd (doublet of doublet of doublet), td (triplet of doublet), and m (multiplet). All NMR measurements were carried out at room temperature.

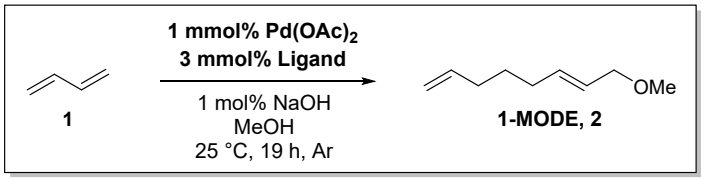
GC measurements were performed on an Agilent HP 6890 with a HP5 column. GC conversion and yields were determined using isooctane as internal standard. GC-MS spectra were recorded on a GC-MS Agilent 5973 Network. HRMS measurements were performed using a Waters Xevo G2XS TOF MS. ATR-IR spectra were recorded on a Nicolet iS5 FT-IR equipped with a PIKE Technologies GladiATR (Thermo Fisher).

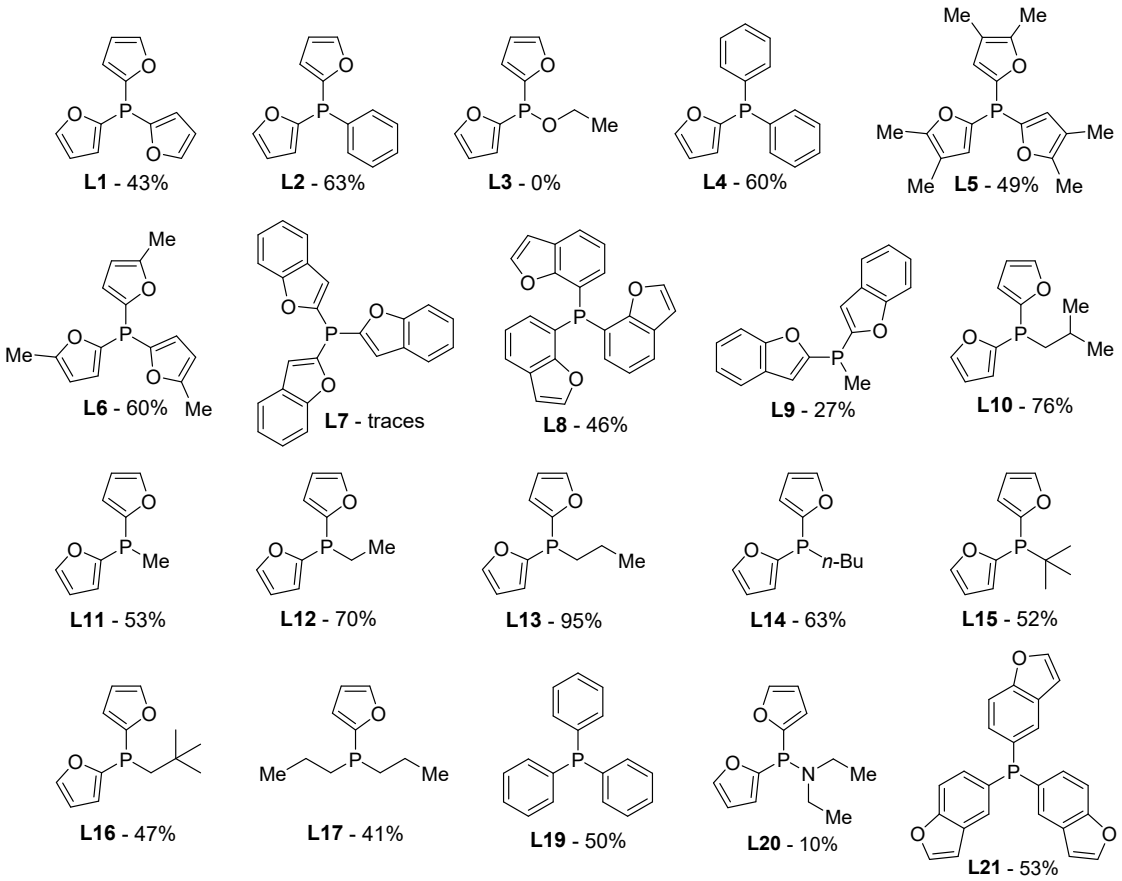
Data were collected on a Bruker Kappa APEX II Duo diffractometer. The structure was solved by intrinsic phasing (SHELXT: Sheldrick, G. M. *Acta Cryst.* **2015**, *A71*, 3.) and refined by full-matrix least-squares procedures on F^2 (SHELXL-2019: Sheldrick, G. M. *Acta Cryst.* **2015**, *C71*, 3.). XP (Bruker AXS) was used for graphical representation. CCDC 2339359 contains 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.

2. Screening conditions

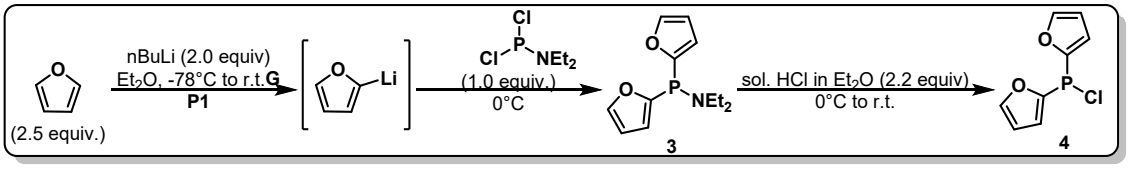
Reaction conditions: $Pd(OAc)_2$ (0.001 mol%), ligand (0.003 mol%), NaOH (1 mol%), MeOH (1.5 mL/1.0 g butadiene), condensed butadiene, Ar, 25 °C, stirring 750 rpm, 19 h. Yields calculated from GC-FID slope with isooctane as internal standard.

Table S1. Screening of ligands for Telomerization reaction.[a]

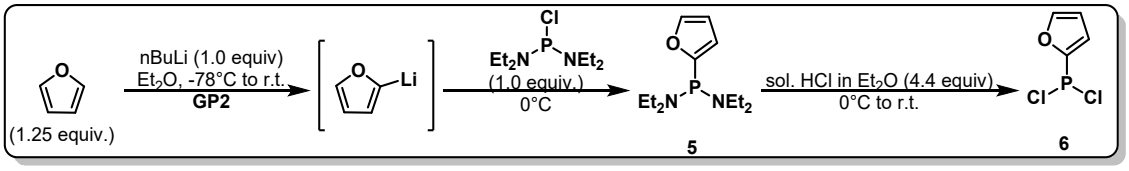




3. Preparation of ligands

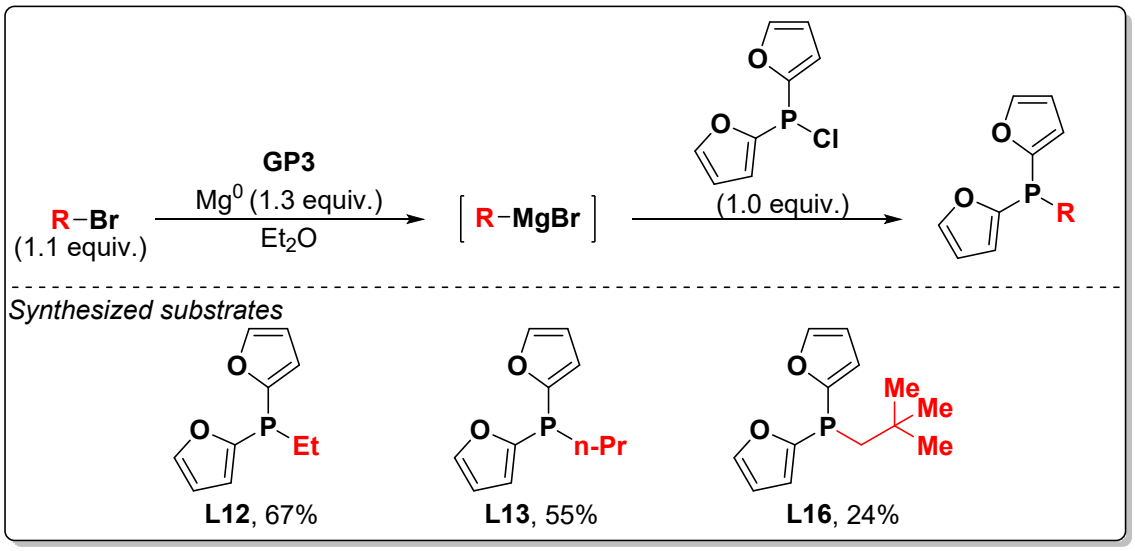


Synthesis of chlorodi(furan-2-yl)phosphane: General Procedure GP1: At -78°C, *n*BuLi (1.6 M, mL, 80 mmol, 2.0 equiv.) was added slowly to a solution of furan (6.8 g, 7.23 mL, 100 mmol, 2.5 equiv.) in Et_2O (50 mL) within 30 min. After the addition was finished, the mixture was warmed up to room temperature, and stirred for 2 h. The yellow solution was again cooled to 0°C, then PCl_2NEt_2 (7.0 g, 40 mmol, 1.0 equiv.) was slowly added. The reaction mixture was stirred overnight and then ethereal HCl (2.0 M, 44 mL, 88 mmol, 2.2 equiv.) was added at 0°C, and stirred for 3 h. The resulting precipitate was filtered off over Celite®. The ether and excess furan were removed under vacuum to yield crude red oil. The red oil was then distilled under vacuum (2.0 mbar) at 90°C to yield colorless oil product in 63% yield.[1]

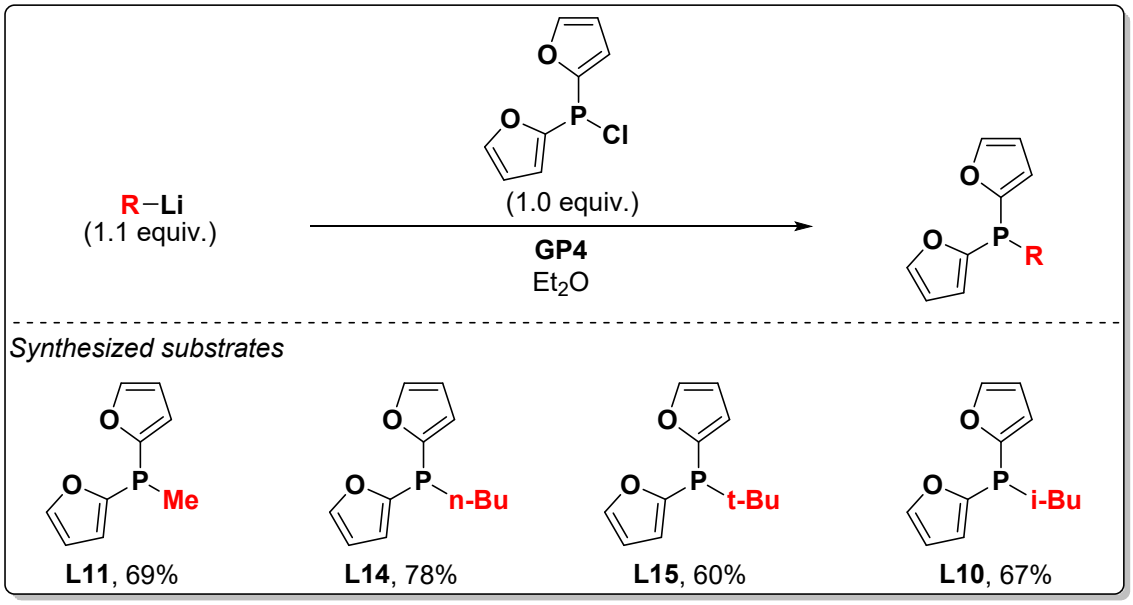


Synthesis of dichloro(furan-2-yl)phosphane: General Procedure GP2: At -78°C, *n*BuLi (1.6 M, 25 mL, 40 mmol, 1.0 equiv.) was added slowly to a solution of furan (3.4 g, 3.62 mL, 50 mmol, 1.25 equiv.) in Et_2O (50 mL) within 30 min. After the addition was finished, the mixture was warmed up to room temperature, and stirred for 2 h. The yellow solution was again cooled to 0°C, then PCl_2NEt_2 (7.0 g, 40 mmol, 1.0 equiv) was slowly added. The reaction mixture was stirred

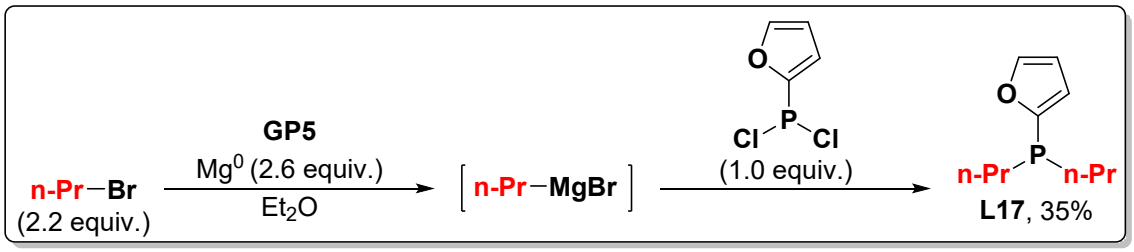
overnight and then ethereal HCl (2.0 M, 88 mL, 176 mmol, 4.4 equiv.) was added at 0°C, and stirred for 3 h. The resulting precipitate was filtered off over Celite®. The ether and excess furan were removed under vacuum to yield crude red oil. The red oil was then distilled under vacuum (1 mbar) at 40°C to yield colorless oil product in 52% yield.[1]



Synthesis of di(furan-2-yl)(alkyl)phosphane ligands: General Procedure GP3: Dry and freshly activated magnesium powder (0.158 g, 6.5 mmol, 1.3 equiv.) was added to a round bottom flask and the system was flamed under vacuum. After cooling down the system, Et_2O (15 mL, 0.33 mol/L) was added under Argon. To this stirring solution, bromoalkyl (1.1 equiv., 5.5 mmol) was added dropwise. The reaction was stirred for 2h at rt, while it was possible to see consumption of powder magnesium and evolution of bubbles (if this is not visible, one can warm up the reactional mixture with hands or with slightly warm water). Then, it was cooled down to -78°C and chlorodi(furan-2-yl)phosphane (1.028 g, 5 mmol, 1.0 equiv.) was added dropwise. The reaction was slowly warmed up to rt and it was stirred overnight. After this period, the reaction was filtered in a 22 µL filter under Argon, the solvent was removed under vacuum, and distillation under vacuum afforded the desired product as a colorless oil.

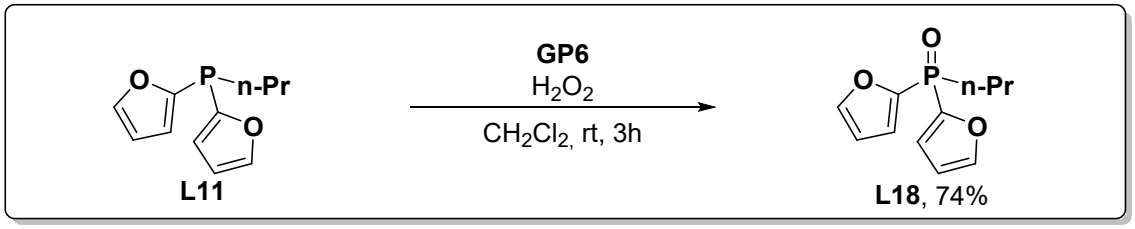


Synthesis of di(furan-2-yl)(alkyl)phosphane ligands: General Procedure GP4: Alkyl lithium (1.1 equiv.) was added under argon to a solution of chlorodi(furan-2-yl)phosphane (1.028 g, 5 mmol, 1.0 equiv.) in Et_2O (15 mL, 0.33 mol/L) at -78°C and it was stirred for 2h. The reaction was slowly warmed up to rt and it was stirred overnight. After this period, the reaction was filtered in a 22 µL filter under Argon, the solvent was removed under vacuum, and distillation under vacuum afforded the desired product as a colorless oil.



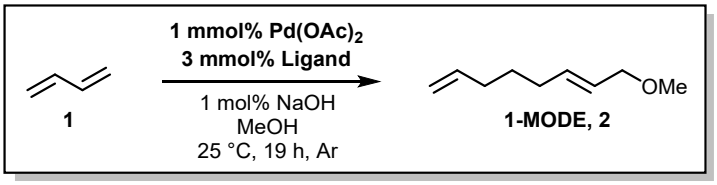
Synthesis of furan-2-yldipropylphosphane L15: General Procedure GP5: Dry and freshly activated magnesium powder (0.316 g, 13.0 mmol, 2.6 equiv.) was added to a round bottom flask and the system was flamed under vacuum. After cooling down the system, Et_2O (15 mL, 0.33 mol/L) was added under Argon. To this stirring solution, bromoalkyl (2.2 equiv., 11.0 mmol) was added dropwise. The reaction was stirred for 2h at rt, while it was possible to see consumption of powder magnesium and evolution of bubbles (if this is not visible, one can warm up the reactional mixture with hands or with slightly warm water). Then, it was

cooled down to -78°C and chlorodi(furan-2-yl)phosphane (0.8447 g, 5 mmol, 1.0 equiv.) was added dropwise. The reaction was slowly warmed up to rt and it was stirred overnight. After this period, the reaction was filtered in a 22 µL filter under Argon, the solvent was removed under vacuum, and distillation under vacuum afforded the desired product as a colorless oil.



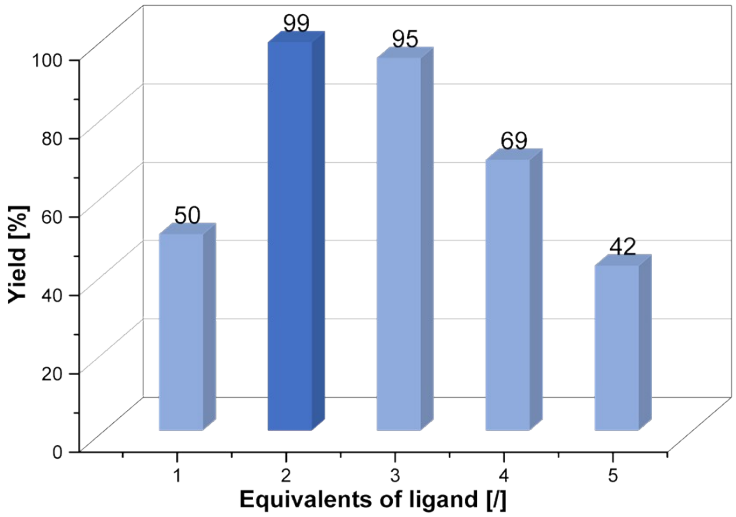
Synthesis of di(furan-2-yl)(propyl)phosphine oxide X: General Procedure GP6: to a solution of di(furan-2-yl)(propyl)phosphine **L11** (1.0 equiv., 1.7 mmol) in dichloromethane (~15 mL) in a flask with a magnetic stirred bar was slowly added aqueous solution of H_2O_2 (70 equiv., 30 wt%). The mixture was stirred for 3 hours at room temperature. After that time, the layers were separated, and the organic phase was washed with water (2x 30 mL) and it was dried over Na_2SO_4. The solvent was evaporated under reduced pressure and the crude was purified by column chromatography, resulting in the desired product in 75% yield as a white solid.[2]

4. Telomerization reaction



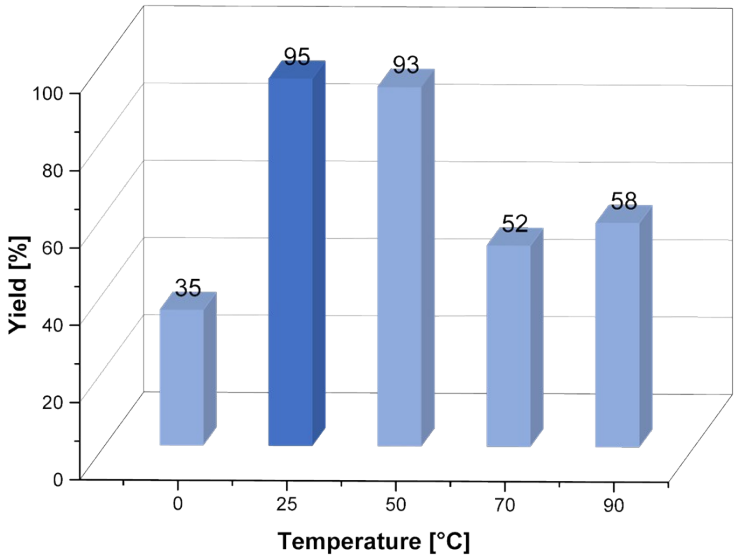
General procedure for telomerization reaction: $Pd(OAc)_2$ (1.3 mg) and ligand **L13** (3.6 mg) were dissolved in methanol (2 mL) and stirred under argon for 10 minutes. Then, 0.001 mol% of $Pd(OAc)_2$ from the previous solution was transferred into a 50 mL stainless steel Parr autoclave. NaOMe (1 mol% solution in methanol) was also added to the autoclave and then it was cooled with dry ice. Methanol was added until it reached the proportion of 1.5 mL/1.0 g of 1,3-butadiene. 1,3-Butadiene (exactly 4 g) was condensed in a separated 75 mL pressure cylinder (mass control) and it was transferred under argon to the cooled autoclave. The autoclave was warmed up to room temperature and it was stirred for 19 hours. Then, internal standard (isooctane) was added to the reaction and the yield of telomerization products was determined by GC-FID.

Table S2. Screening of equivalents of ligand (L:M ratio)



General conditions: [Pd] (0.001 mol%), L13 (1-5 mol%), NaOH (1 mol%), MeOH (1.5 mL/1.0 g butadiene), condensed butadiene, Ar, room temperature, stirring 750 rpm, 19h. Yields calculated from GC slope with isooctane as internal standard.

Table S3. Screening of temperature for Telomerization reaction.



General conditions: [Pd] (0.001 mol%), L13 (0.003 mol%), NaOH (1 mol%), MeOH (1.5 mL/1.0 g butadiene), condensed butadiene, Ar, temperature, stirring 750 rpm, 19h. Yields calculated from GC slope with isooctane as internal standard.

5. Reactional set up

Figure S1 – 1,3-Butadiene bottle connected to container where 1,3-butadiene is condensed.

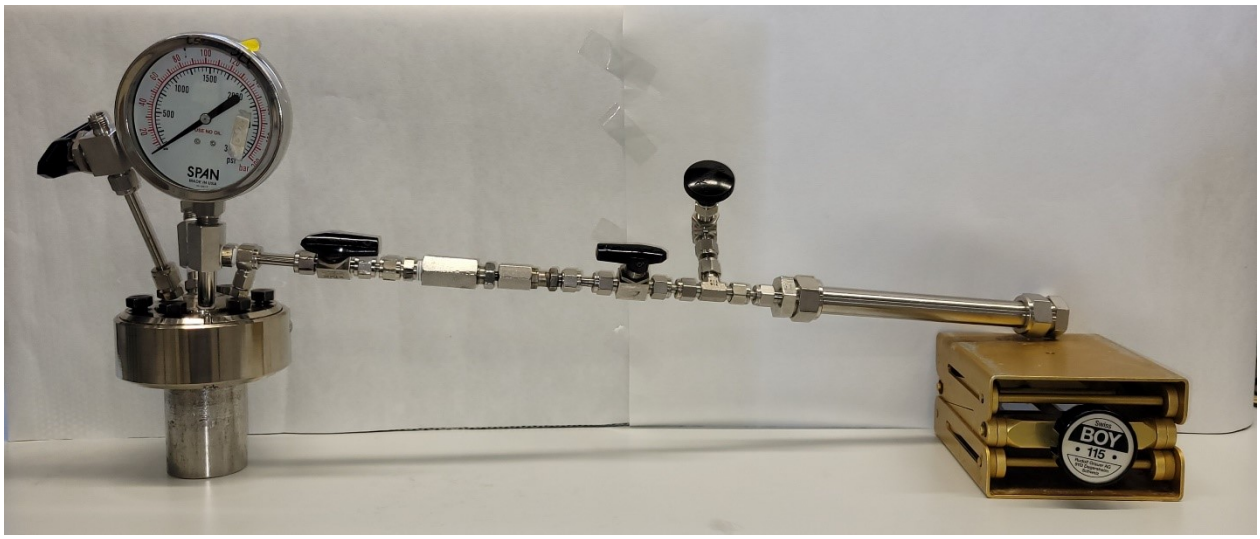
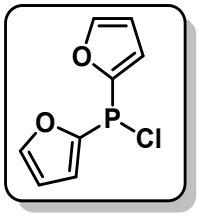


Figure S2 – Container connected to autoclave, for the transference of the 1,3-butadiene.

Figure S3 – Autoclave set for telomerization reaction the 1,3-butadiene.

6. Characterization of the compounds



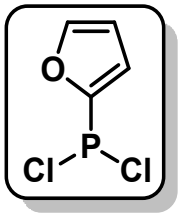
Chlorodi(furan-2-yl)phosphane (4)

Isolated yield: 63% (5.0359 g, 25.11 mmol). Colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (dd, J = 1.8, 0.7 Hz, 2H), 7.03 (ddd, J = 3.4, 1.7, 0.8 Hz, 2H), 6.49 (dt, J = 3.4, 1.9 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 150.50 (d, J = 33.4 Hz), 149.00 (d, J = 3.5 Hz), 123.10 (d, J = 30.8 Hz), 111.27 (d, J = 6.6 Hz).

^{31}P NMR (122 MHz, $CDCl_3$) δ 16.9.



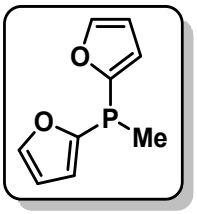
Dichloro(furan-2-yl)phosphane (6)

Isolated yield: 52% (3.5045 g, 20.74 mmol). Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, J = 1.7, 0.7 Hz, 1H), 7.14 (ddd, J = 3.5, 1.5, 0.7 Hz, 1H), 6.53 (ddd, J = 3.5, 2.4, 1.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.41 (d, J = 67.3 Hz), 149.86 (d, J = 3.1 Hz), 122.13 (d, J = 35.1 Hz), 111.34 (d, J = 6.5 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 122.7.



Di(furan-2-yl)(methyl)phosphane (L11)

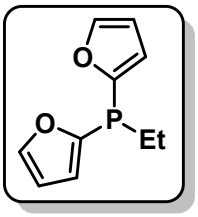
Isolated yield: 69% (340.0 mg, 2.74 mmol). Colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (dd, J = 1.8, 0.8 Hz, 2H), 6.69 (ddd, J = 3.3, 1.7, 0.8 Hz, 2H), 6.38 (ddd, J = 3.2, 1.8, 1.4 Hz, 2H), 1.65 (d, J = 3.9 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 152.7 (d, J = 16.3 Hz), 146.9 (d, J = 1.7 Hz), 119.1 (d, J = 24.3 Hz), 110.7 (d, J = 5.8 Hz), 9.5 (d, J = 3.0 Hz).

^{31}P NMR (122 MHz, $CDCl_3$) δ -70.1.

HRMS (ESI+) m/z calculated for [$C_9H_9O_2PNa^+$] = 181.0413, found 181.0415.



Ethyldi(furan-2-yl)phosphane (L12)

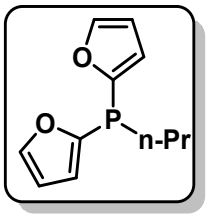
Isolated yield: 67% (652.9 mg, 3.36 mmol). Colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (dd, J = 1.8, 0.8 Hz, 2H), 6.74 (ddd, J = 3.2, 1.9, 0.8 Hz, 2H), 6.39 (dt, J = 3.2, 1.6 Hz, 2H), 2.15 (q, J = 7.6, 2H), 1.05 (dt, J = 18.4, 7.6 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 151.8 (d, J = 17.2 Hz), 146.9 (d, J = 1.4 Hz), 120.2 (d, J = 24.2 Hz), 110.6 (d, J = 6.0 Hz), 18.5, 10.11 (d, J = 15.9 Hz).

^{31}P NMR (122 MHz, $CDCl_3$) δ -57.2.

HRMS (ESI+) m/z calculated for [$C_{10}H_{11}O_2PH^+$] = 195.0570, found 195.0575.



Di(furan-2-yl)(propyl)phosphane (L13)

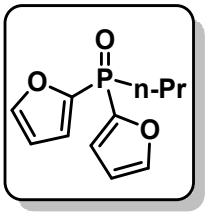
Isolated yield: 55% (570.8 mg, 2.74 mmol). Colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (dd, J = 1.8, 0.8 Hz, 2H), 6.73 (ddd, J = 3.3, 1.9, 0.8 Hz, 2H), 6.38 (ddd, J = 3.3, 1.8, 1.5 Hz, 2H), 2.19 – 2.10 (m, 2H), 1.51 – 1.35 (m, 2H), 1.00 (t, J = 7.3 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 152.0 (d, J = 17.3 Hz), 146.9 (d, J = 1.5 Hz), 120.0 (d, J = 24.6 Hz), 110.6 (d, J = 6.3 Hz), 27.7, 19.45 (d, J = 16.1 Hz), 15.6 (d, J = 13.9 Hz).

^{31}P NMR (122 MHz, $CDCl_3$) δ -62.0.

HRMS (ESI+) m/z calculated for [$C_{11}H_{13}O_2PH^+$] = 209.0726, found 209.0728.



Di(furan-2-yl)(propyl)phosphine oxide (L18)

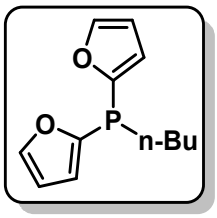
Isolated yield: 74% (276.1 mg, 1.23 mmol). White solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (ddd, J = 2.5, 1.7, 0.7 Hz, 2H), 7.02 (ddd, J = 3.5, 1.8, 0.7 Hz, 2H), 6.43 (ddd, J = 3.5, 1.7, 1.3 Hz, 2H), 2.27 – 2.15 (m, 2H), 1.68 – 1.53 (m, 2H), 0.95 (td, J = 7.4, 1.1 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 147.9 (d, J = 7.7 Hz), 147.4 (d, J = 138.4 Hz), 121.7 (d, J = 18.6 Hz), 110.9 (d, J = 8.4 Hz), 31.5 (d, J = 80.1 Hz), 15.3 (d, J = 16.1 Hz), 14.7 (d, J = 4.1 Hz).

^{31}P NMR (122 MHz, $CDCl_3$) δ 12.2.

HRMS (ESI+) m/z calculated for [$C_{11}H_{13}O_3PH^+$] = 225.0675, found 225.0672.



Butyldi(furan-2-yl)phosphane (L14)

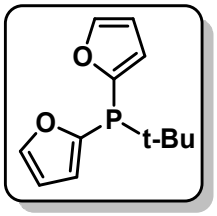
Isolated yield: 78% (873.6 mg, 3.9 mmol). Colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (dd, J = 1.8, 0.7 Hz, 2H), 6.72 (ddd, J = 3.2, 1.9, 0.8 Hz, 2H), 6.38 (dt, J = 3.3, 1.6 Hz, 2H), 2.20 – 2.10 (m, 2H), 1.39 (ddt, J = 6.3, 5.2, 2.0 Hz, 4H), 0.93 – 0.83 (m, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 152.0 (d, J = 17.4 Hz), 146.9 (d, J = 1.5 Hz), 120.0 (d, J = 24.6 Hz), 110.6 (d, J = 6.2 Hz), 28.1 (d, J = 15.3 Hz), 25.17, 24.0 (d, J = 13.7 Hz), 13.8.

^{31}P NMR (122 MHz, $CDCl_3$) δ -61.3.

HRMS (ESI+) m/z calculated for $[C_{12}H_{15}O_2PH^+]$ = 223.0883, found 223.0886.



***Tert*-butyldi(furan-2-yl)phosphane (L15)**

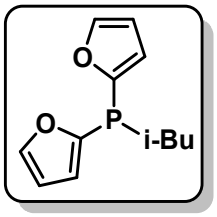
Isolated yield: 60% (666.66 mg, 3.0 mmol). Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dt, J = 1.8, 0.6 Hz, 2H), 6.83 (ddd, J = 3.1, 2.2, 0.8 Hz, 2H), 6.42 (dt, J = 3.2, 1.6 Hz, 2H), 1.11 (d, J = 14.0 Hz, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.9 (d, J = 15.6 Hz), 147.0 (d, J = 1.8 Hz), 122.2 (d, J = 23.0 Hz), 110.5 (d, J = 6.6 Hz), 32.4 (d, J = 5.9 Hz), 28.3 (d, J = 14.9 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ -29.7.

HRMS (ESI+) m/z calculated for $[C_{12}H_{15}O_2PH^+]$ = 223.0883, found 223.0886.



Di(furan-2-yl)(isobutyl)phosphane (L10)

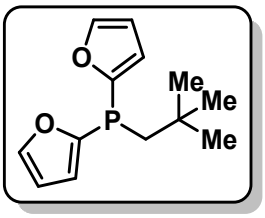
Isolated yield: 67% (744.4 mg, 3.35 mmol). Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (dd, J = 1.8, 0.8 Hz, 2H), 6.71 (ddd, J = 3.3, 2.0, 0.8 Hz, 2H), 6.37 (dt, J = 3.3, 1.7 Hz, 2H), 2.12 (d, J = 7.0 Hz, 2H), 1.71 – 1.58 (m, 1H), 0.99 (dd, J = 6.6, 0.7 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.2 (d, J = 17.4 Hz), 146.9 (d, J = 1.4 Hz), 119.9 (d, J = 25.2 Hz), 110.6 (d, J = 6.3 Hz), 35.1 (d, J = 1.8 Hz), 26.2 (d, J = 14.1 Hz), 23.9 (d, J = 9.9 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ -64.9.

HRMS (ESI+) m/z calculated for $[C_{12}H_{15}O_2PH^+]$ = 223.0883, found 223.0886.



Di(furan-2-yl)(neopentyl)phosphane (L16)

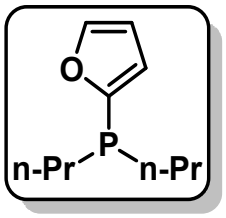
Isolated yield: 24% (279.1 g, 1.18 mmol). Colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (dd, J = 1.8, 0.7 Hz, 2H), 6.69 (ddd, J = 3.3, 2.0, 0.8 Hz, 2H), 6.36 (dt, J = 3.3, 1.7 Hz, 2H), 2.24 (d, J = 3.3 Hz, 2H), 0.97 (d, J = 1.1 Hz, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 152.8 (d, J = 16.3 Hz), 146.7 (d, J = 1.5 Hz), 119.6 (d, J = 25.8 Hz), 110.7 (d, J = 6.4 Hz), 40.7 (d, J = 4.2 Hz), 31.1 (d, J = 13.2 Hz), 30.5 (d, J = 9.1 Hz).

^{31}P NMR (122 MHz, $CDCl_3$) δ -69.1.

HRMS (ESI+) m/z calculated for [$C_{13}H_{17}O_2PH^+$] = 237.1039, found 237.1041.



Furan-2-yldipropylphosphane (L17)

Isolated yield: 35% (320.9 mg, 1.74 mmol). Colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (dd, J = 1.8, 0.7 Hz, 1H), 6.66 (ddd, J = 3.2, 2.0, 0.7 Hz, 1H), 6.36 (ddd, J = 3.1, 1.8, 1.1 Hz, 1H), 1.90 – 1.76 (m, 2H), 1.59 (dddd, J = 13.4, 9.7, 6.0, 3.6 Hz, 2H), 1.50 – 1.29 (m, 4H), 0.96 (t, J = 7.3 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 154.9 (d, J = 28.4 Hz), 146.4, 119.6 (d, J = 24.4 Hz), 110.3 (d, J = 5.9 Hz), 29.1 (d, J = 6.4 Hz), 19.7 (d, J = 13.6 Hz), 15.9 (d, J = 12.2 Hz).

^{31}P NMR (122 MHz, $CDCl_3$) δ -45.1.

HRMS (ESI+) m/z calculated for [$C_{10}H_{17}OPH^+$] = 185.1090, found 185.1088.

(*E*)-8-Methoxyocta-1,6-diene (2)

Yield (CG-FID): 95%.

Isolation: The methanol was removed from the crude in the rotatory evaporator, furnishing the desired product as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.87 – 5.63 (m, 2H), 5.54 (dtt, J = 15.3, 6.1, 1.2 Hz, 1H), 5.05 – 4.90 (m, 2H), 3.86 (dq, J = 5.9, 0.9 Hz, 2H), 3.31 (s, 3H), 2.12 – 2.00 (m, 4H), 1.55 – 1.42 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 138.7, 134.6, 126.5, 114.7, 73.4, 57.8, 33.3, 31.8, 28.4.

7. X-Ray Diffraction

Crystal data of **L18** (CCDC 2339359): $C_{11}H_{13}O_3P$, M = 224.18, monoclinic, space group $P2_1$, a = 10.5361(4), b = 8.4344(3), c = 12.6771(5) Å, b = 98.8044(13)°, V = 1113.28(7) Å^3, T = 150(2) K, Z = 4, 14767 reflections measured, 4055 independent reflections (R_{int} = 0.0272), final R values ($I > 2\sigma(I)$): R_1 = 0.0250, wR_2 = 0.0681, final R values (all data): R_1 = 0.0257, wR_2 = 0.0692, 273 parameters.

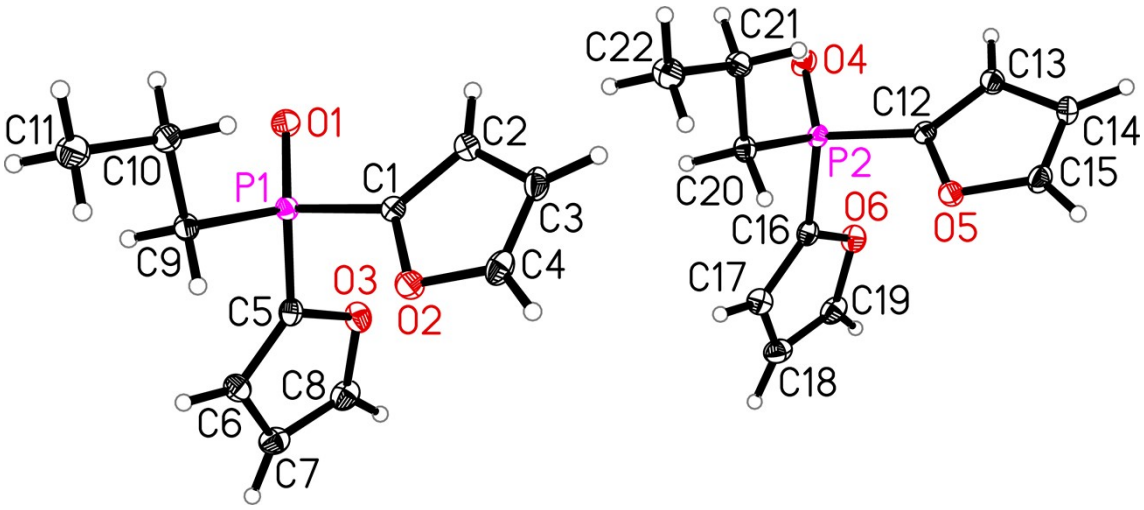


Figure S4. Molecular structure of **L16**. Displacement ellipsoid corresponds to 50% probability.

8. NMR Spectra

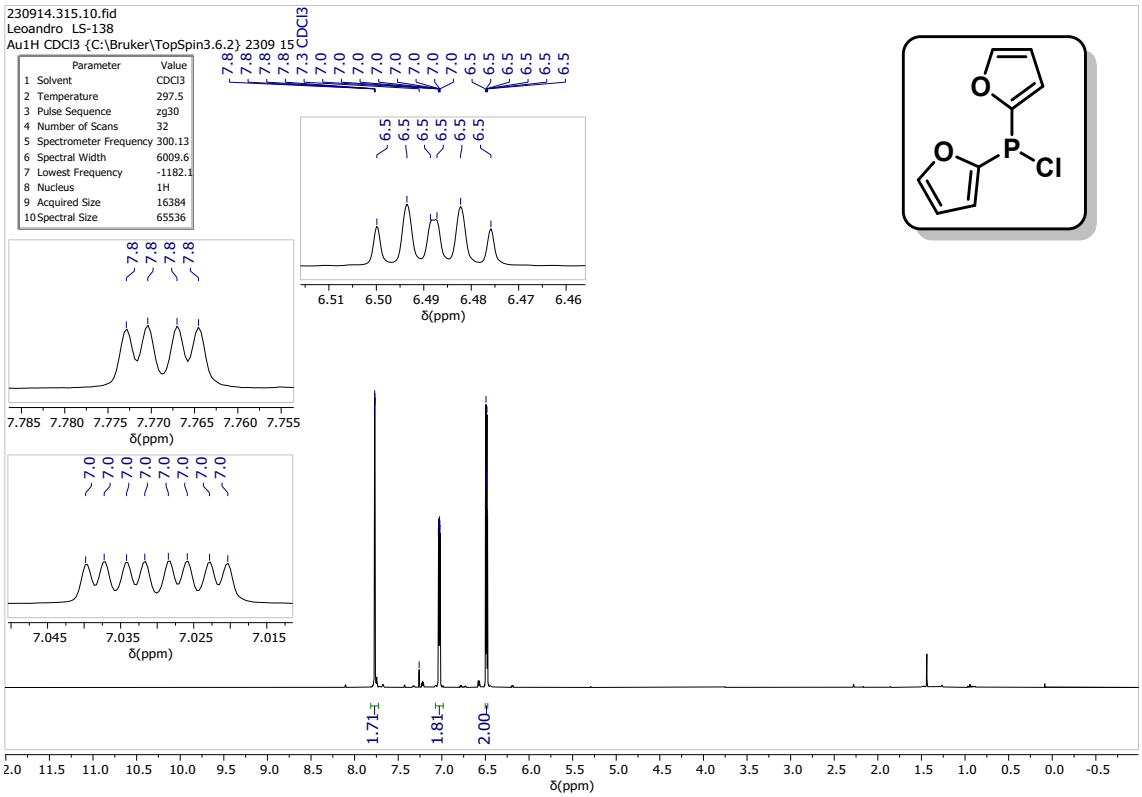


Figure S5: ^{1}H NMR of compound **(4)**.

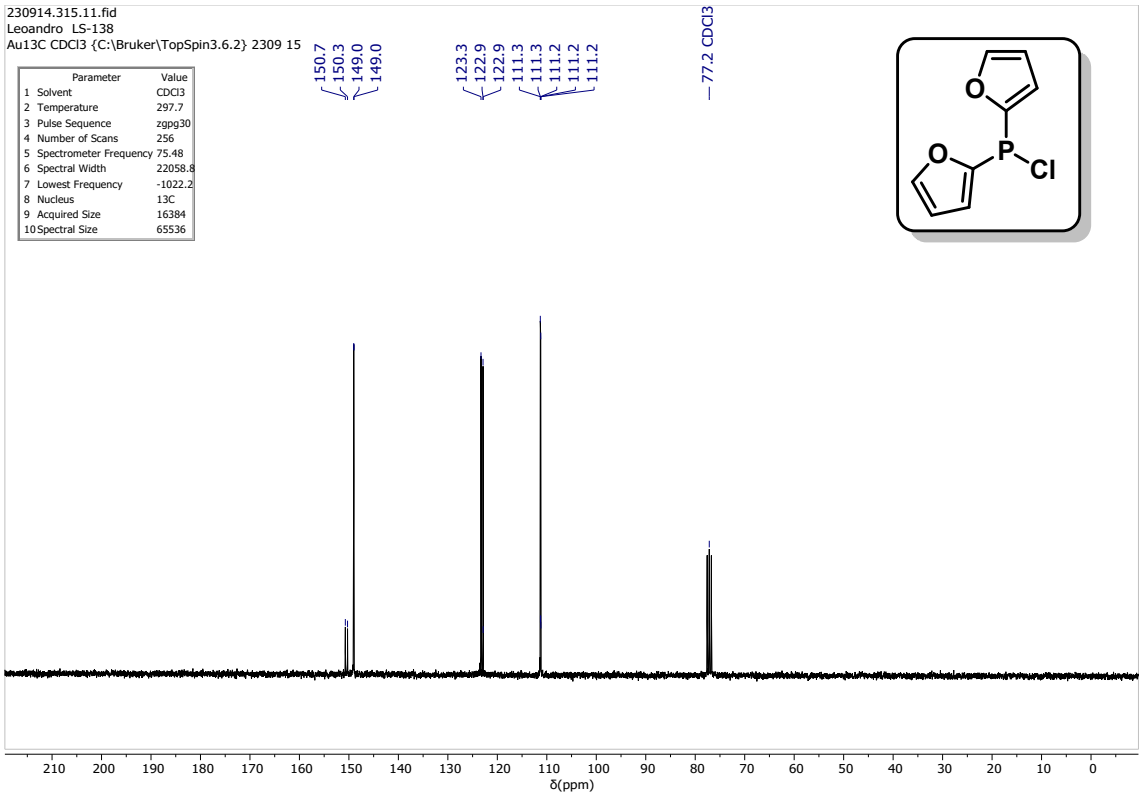


Figure S6: ^{13}C NMR of compound **(4)**.

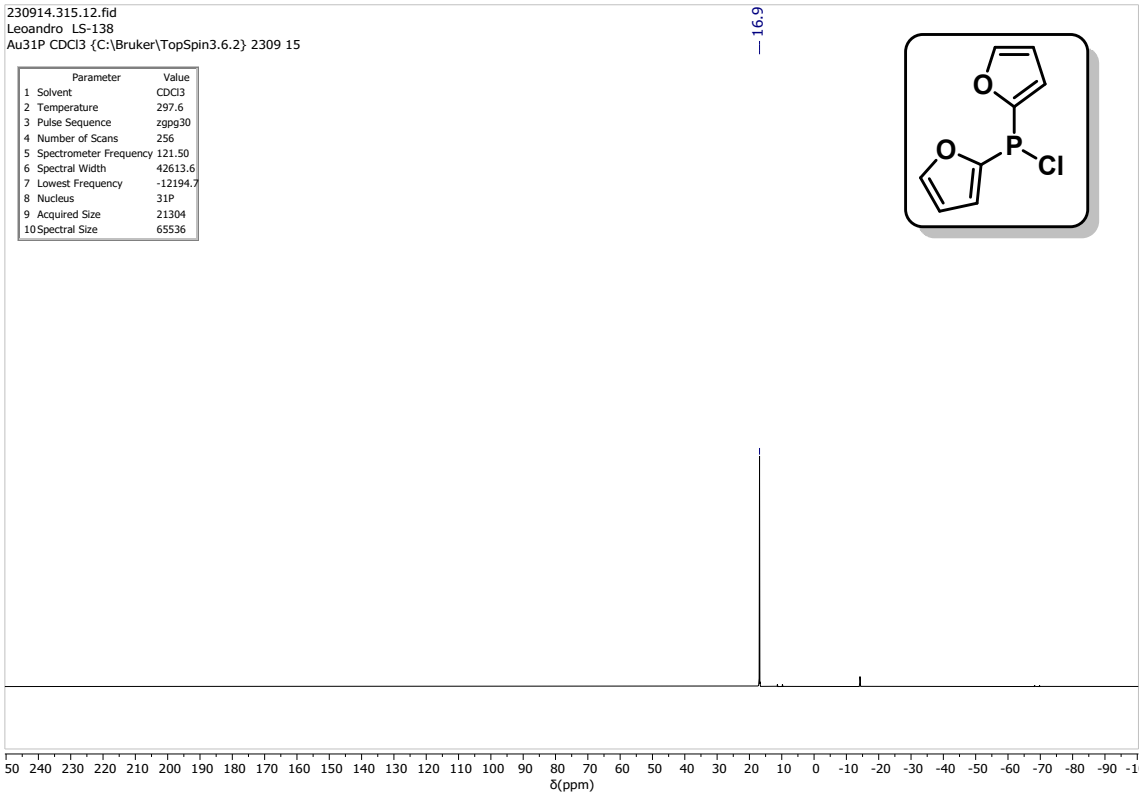


Figure S7: ^{31}P NMR of compound **(4)**.

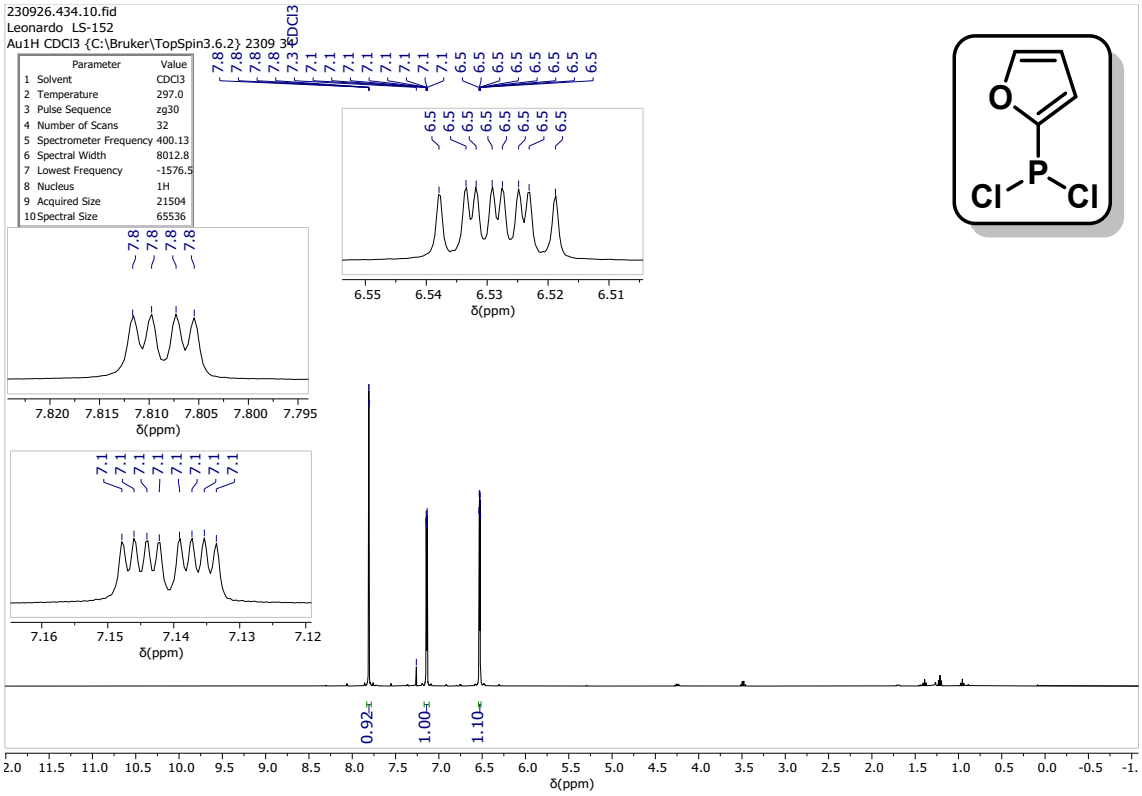


Figure S8: ^{1}H NMR of compound **(6)**.

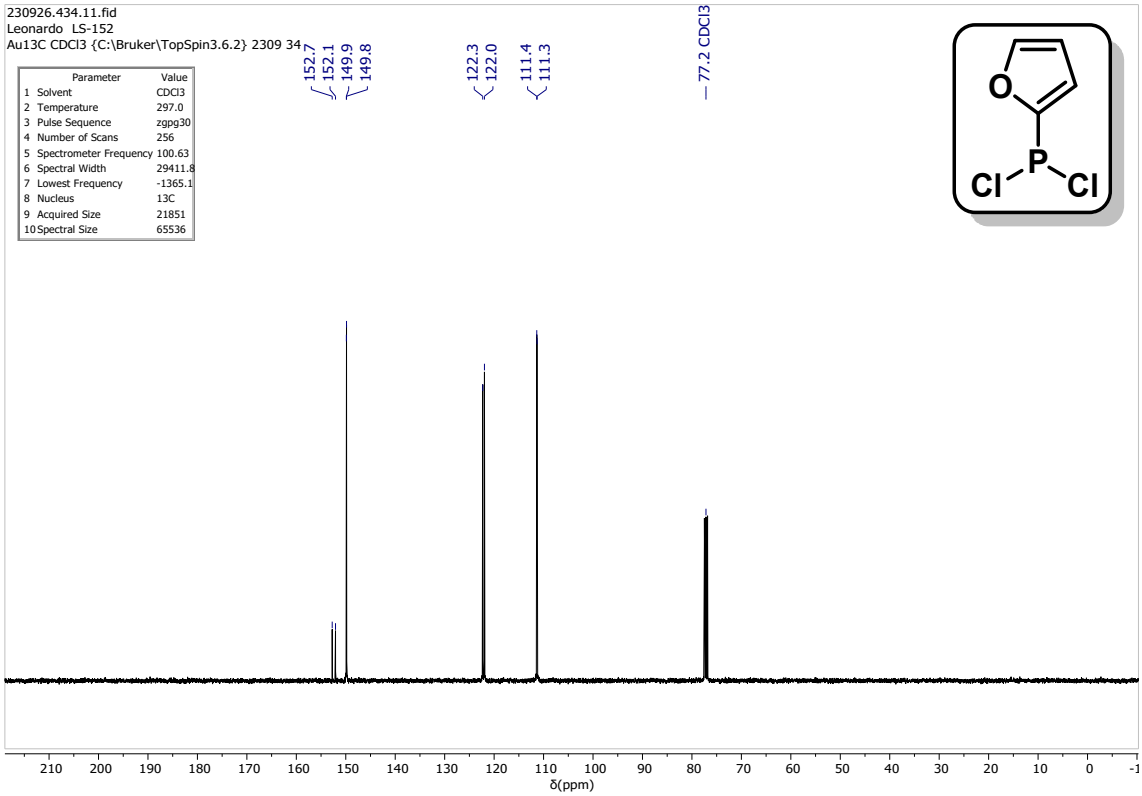


Figure S9: ^{13}C NMR of compound **(6)**.

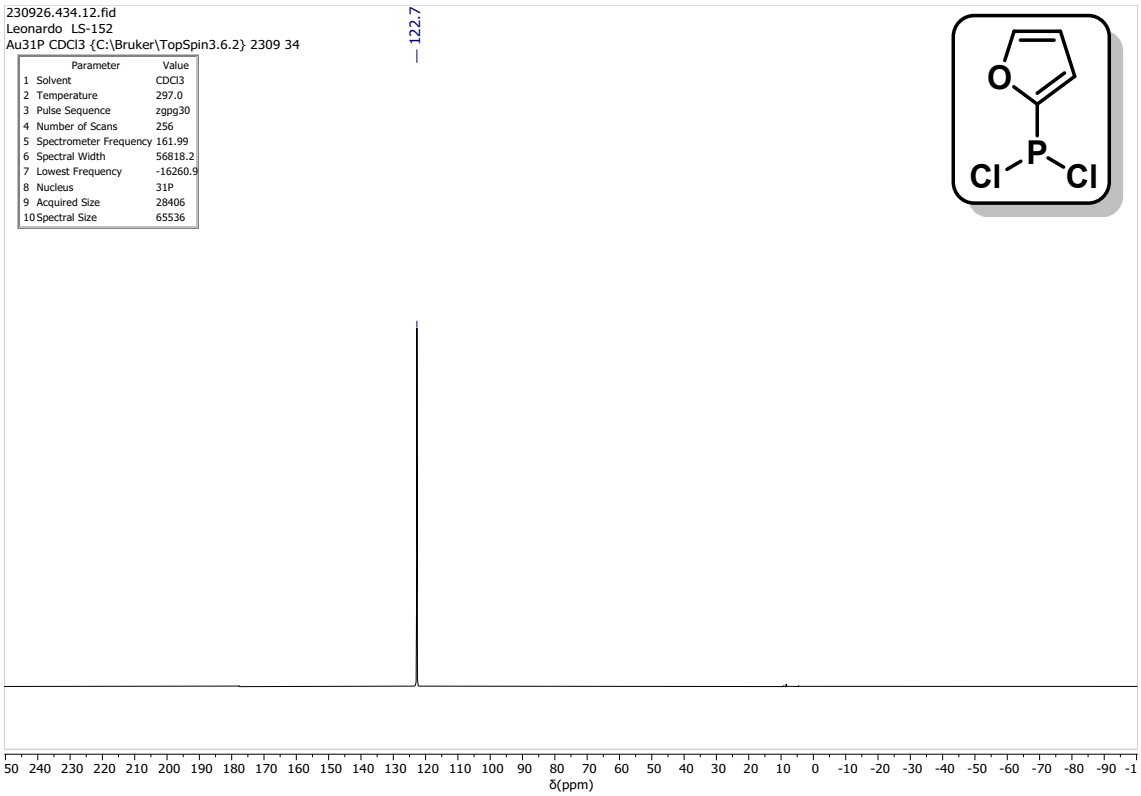


Figure S10: ^{31}P NMR of compound **(6)**.

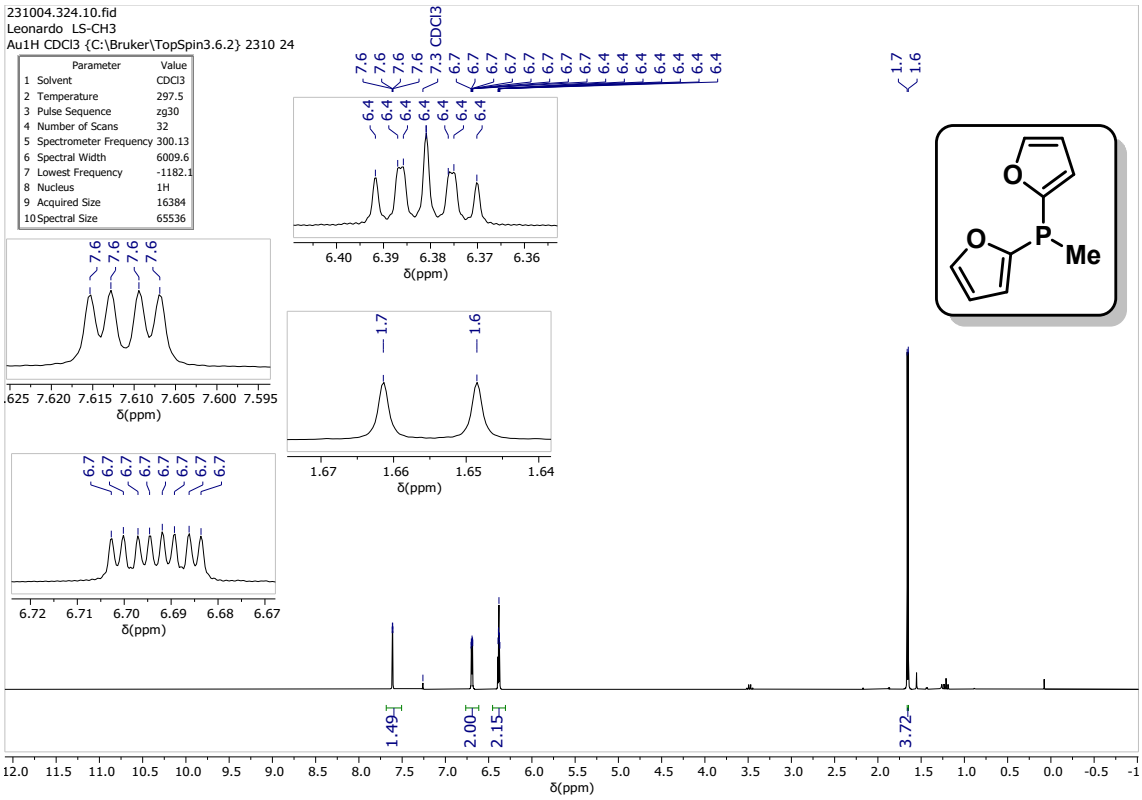


Figure S11: ^{1}H NMR of compound **(L11)**.

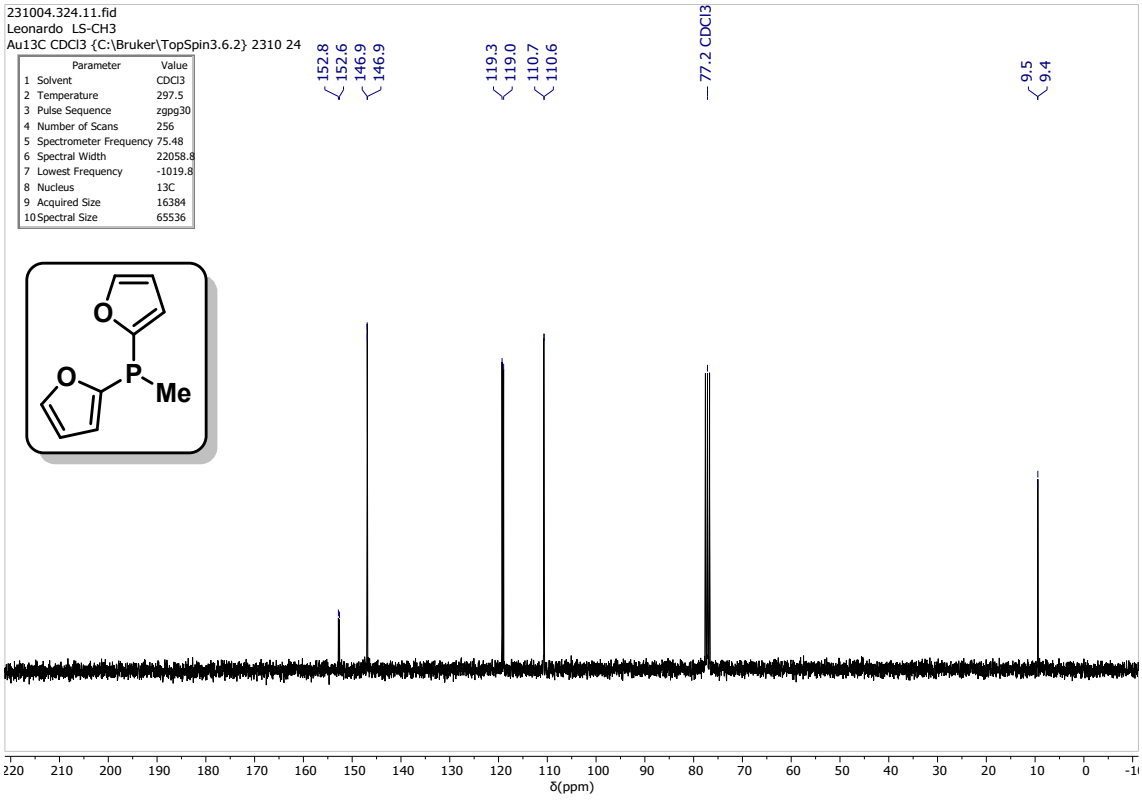


Figure S12: ^{13}C NMR of compound **(L11)**.

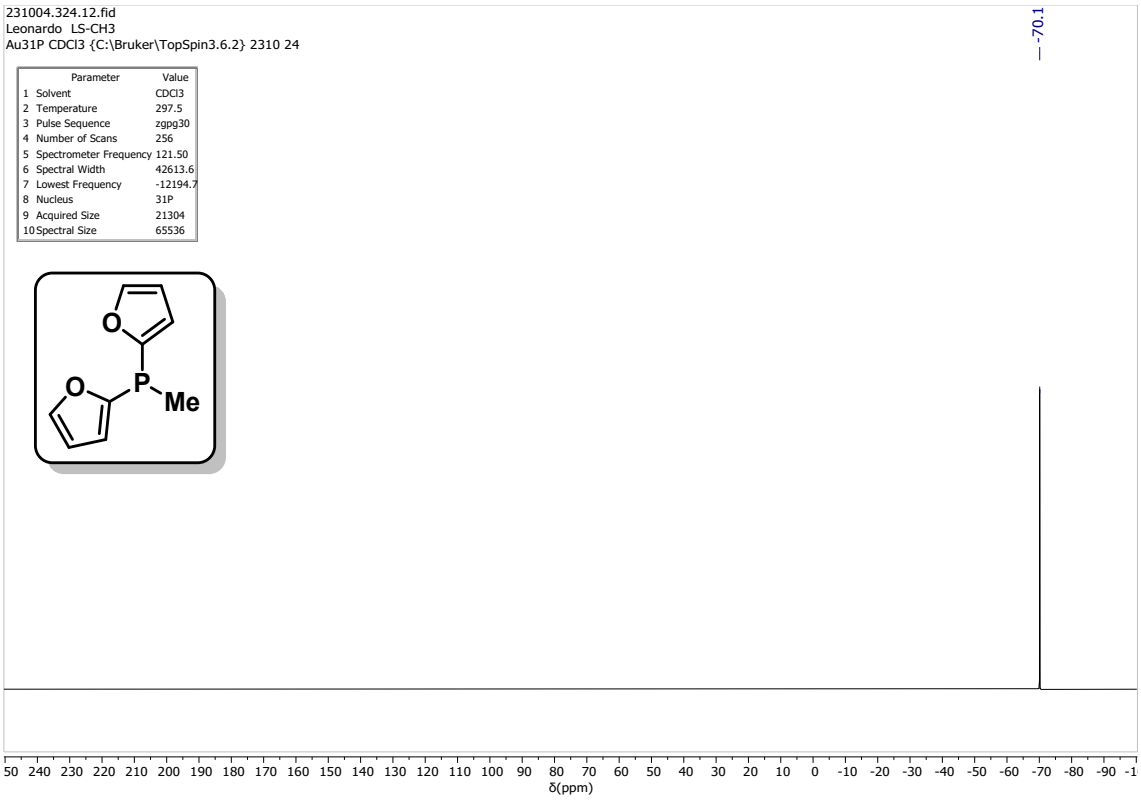


Figure S13: ^{31}P NMR of compound **(L11)**.

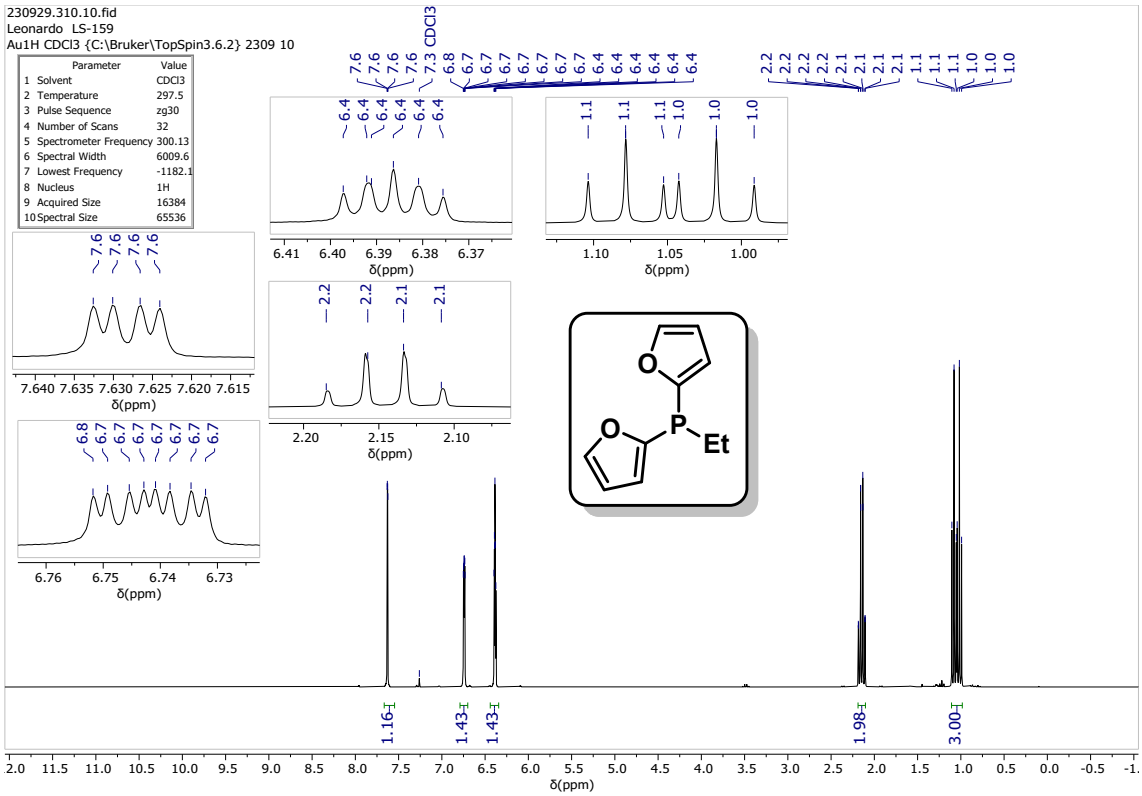


Figure S14: ^{1}H NMR of compound **(L12)**.

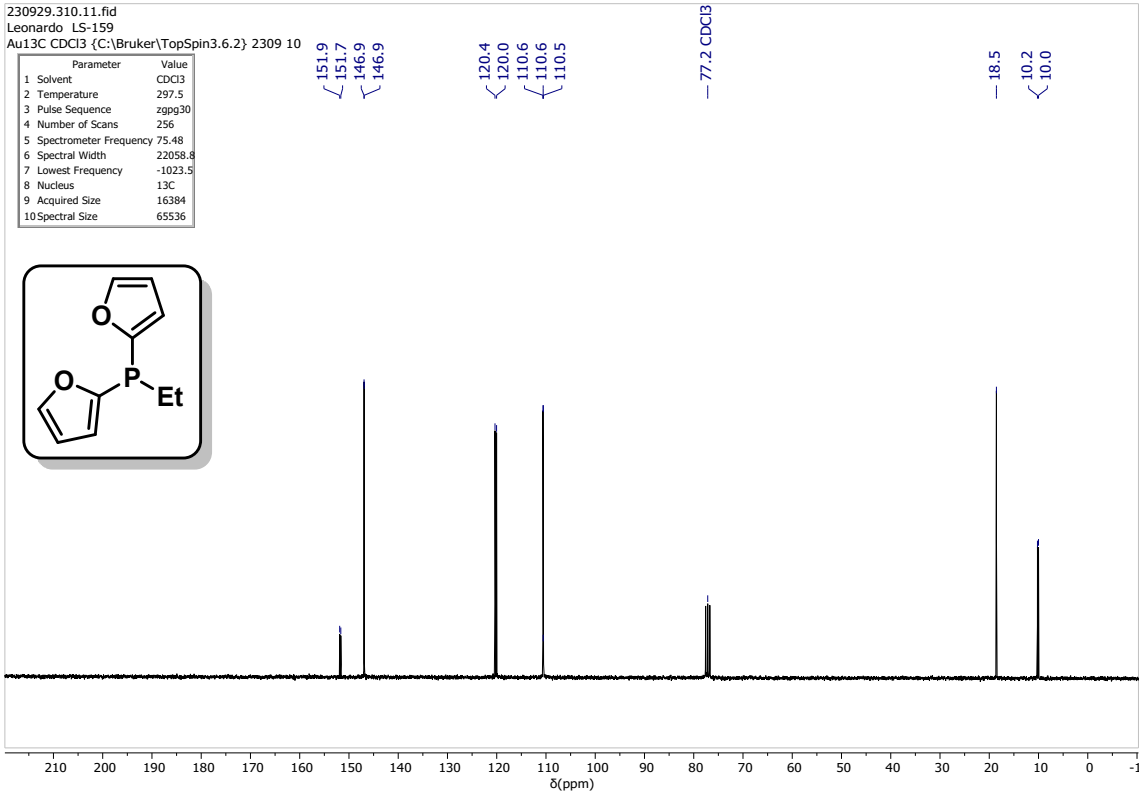


Figure S15: ^{13}C NMR of compound **(L12)**.

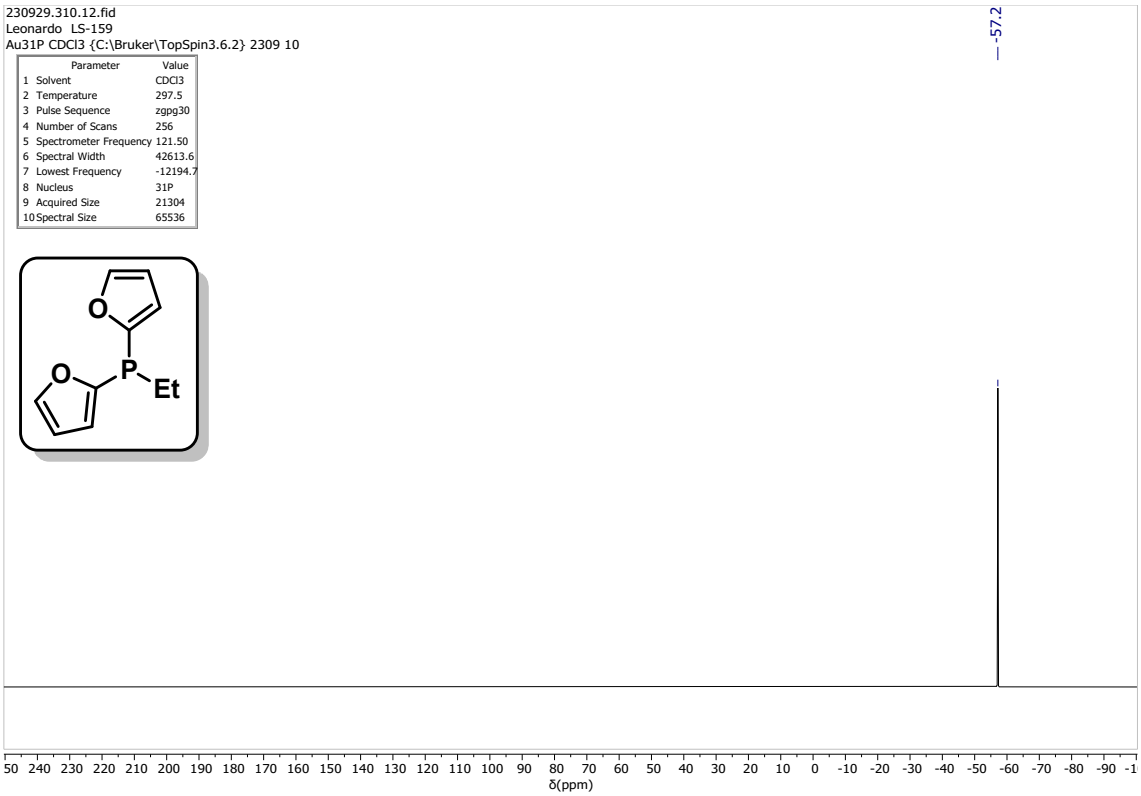


Figure S16: ^{31}P NMR of compound **(L12)**.

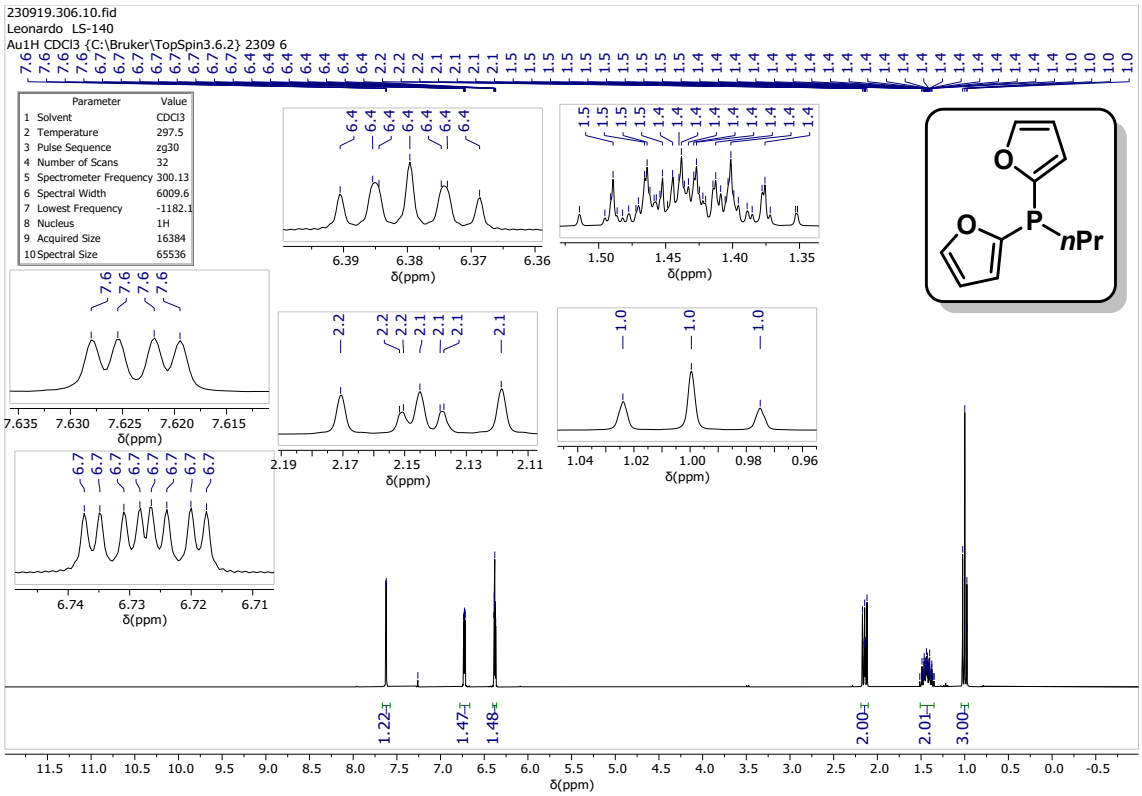


Figure S17: ^{1}H NMR of compound **(L13)**.

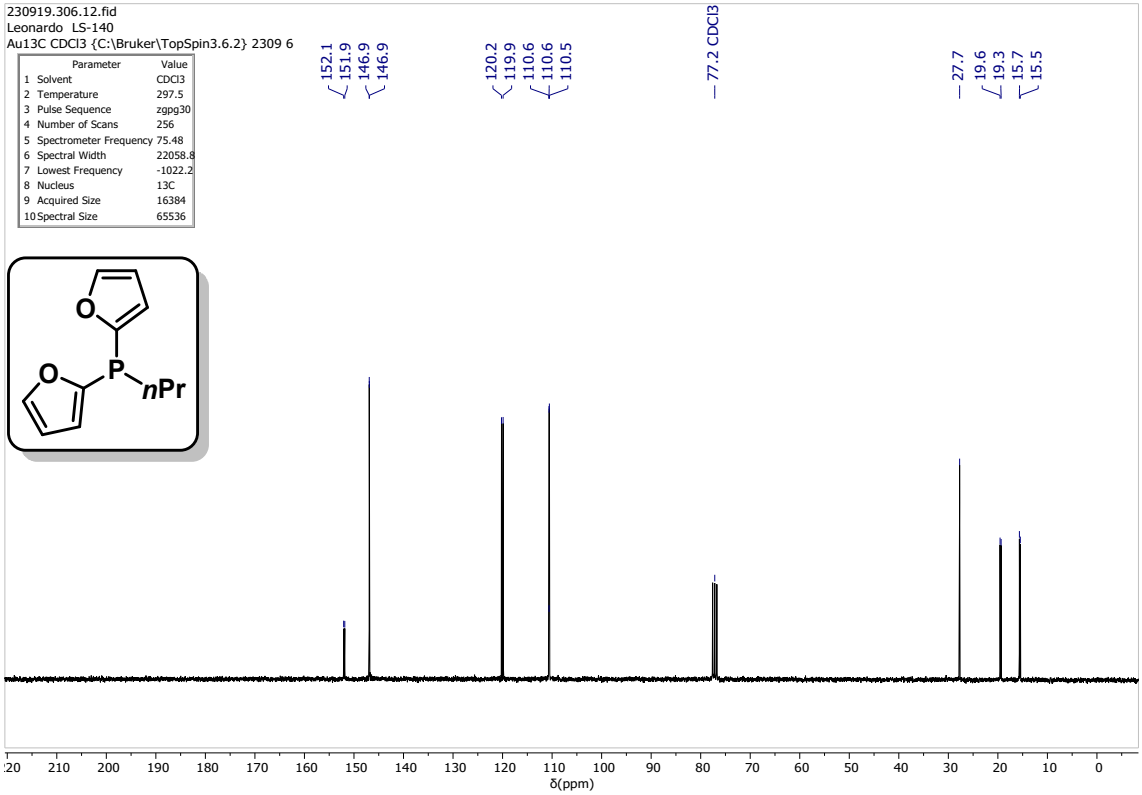


Figure S18: ^{13}C NMR of compound **(L13)**.

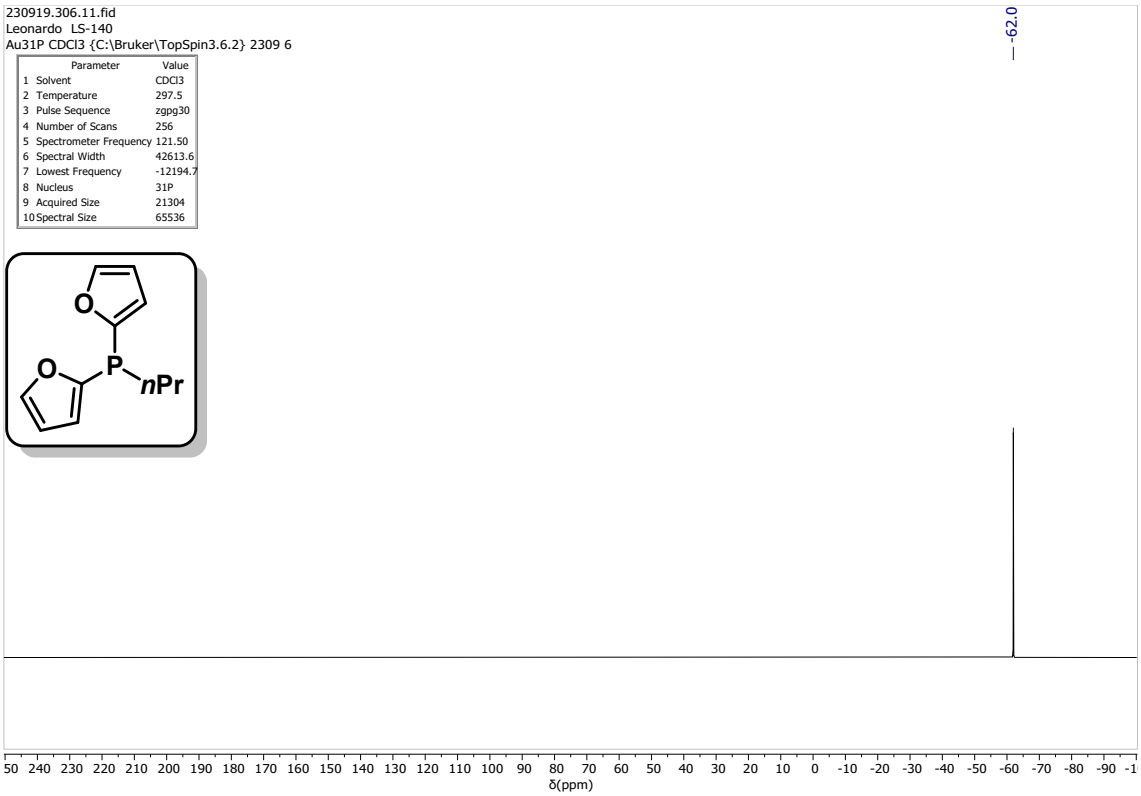


Figure S19: ^{31}P NMR of compound **(L13)**.

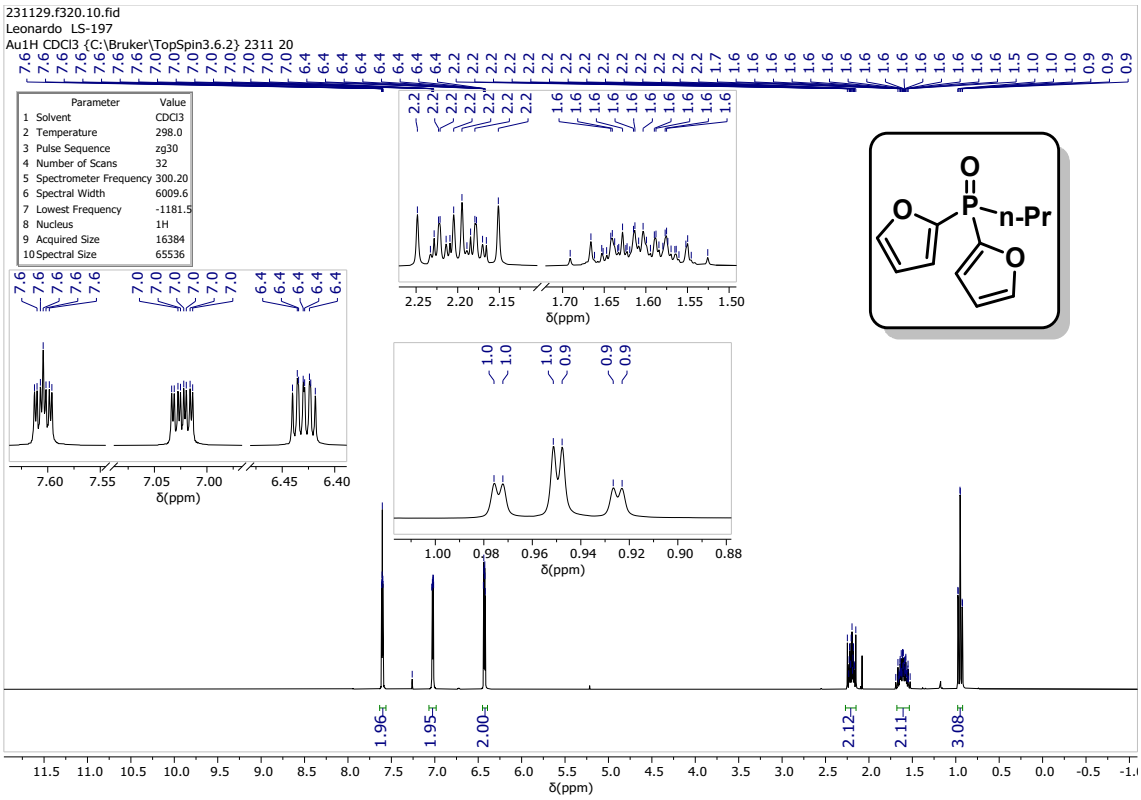


Figure S20: ^{1}H NMR of compound **(L18)**.

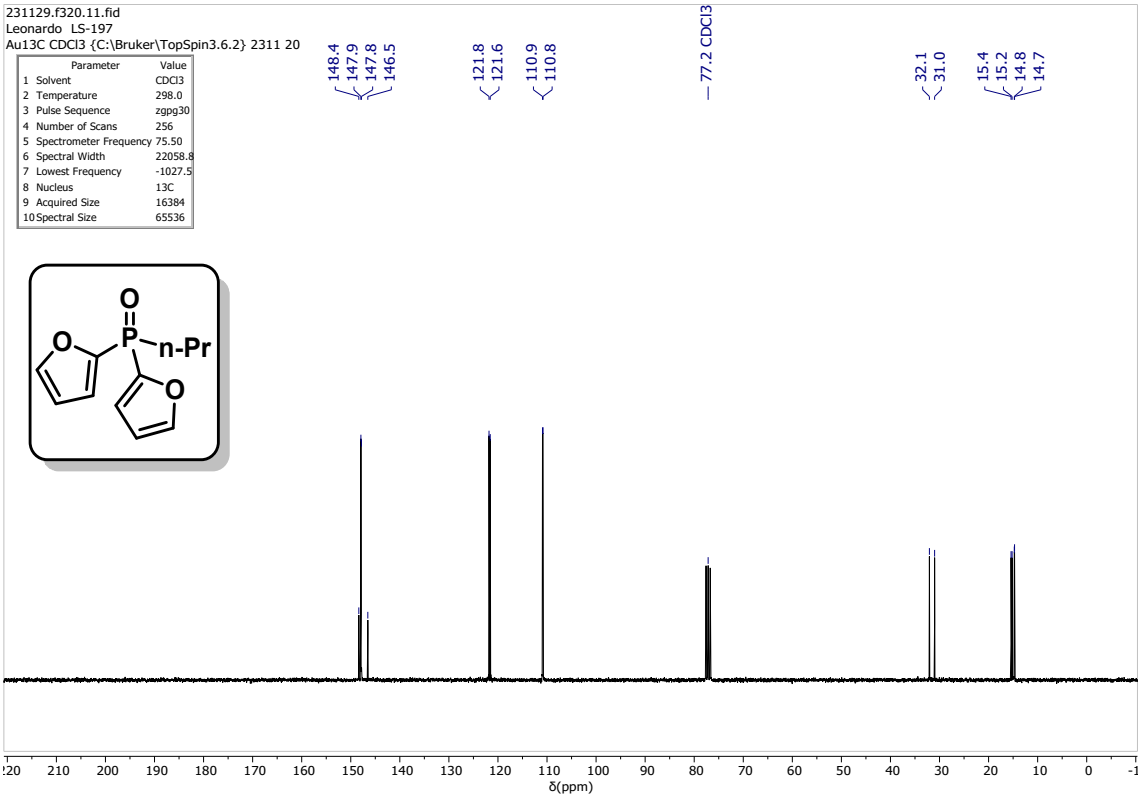


Figure S21: ^{13}C NMR of compound **(L18)**.

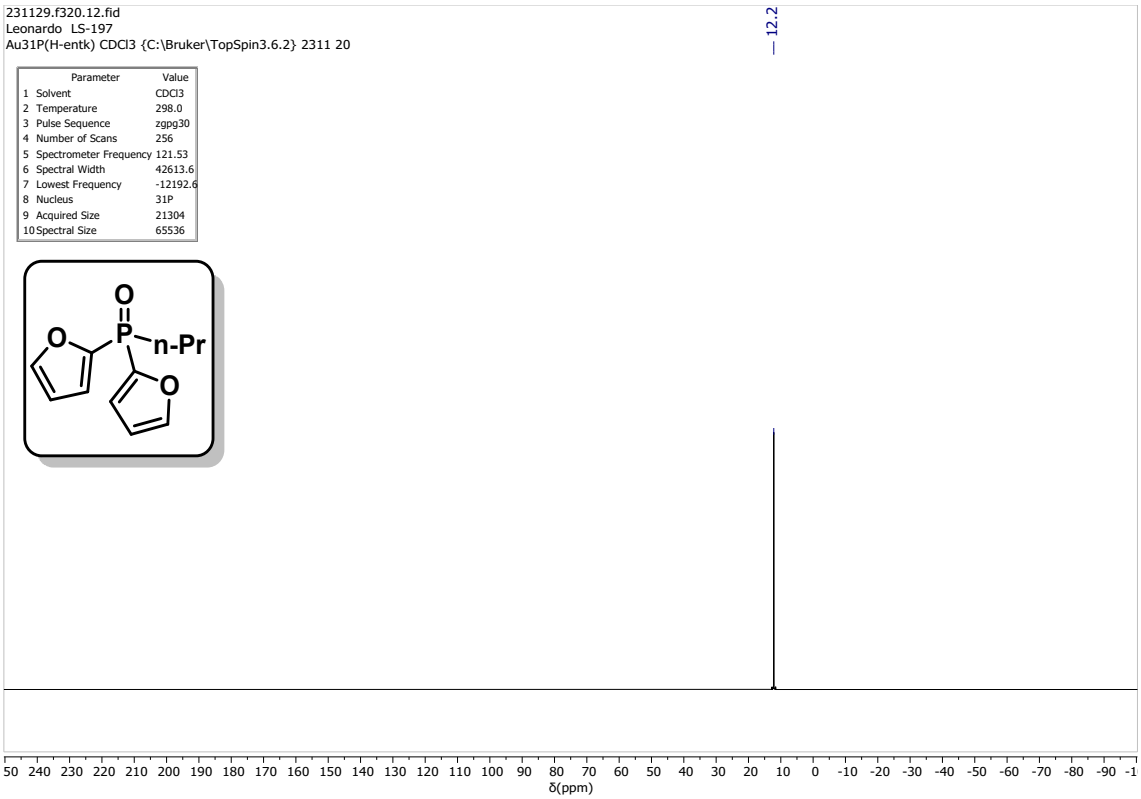


Figure S22: ^{31}P NMR of compound **(L18)**.

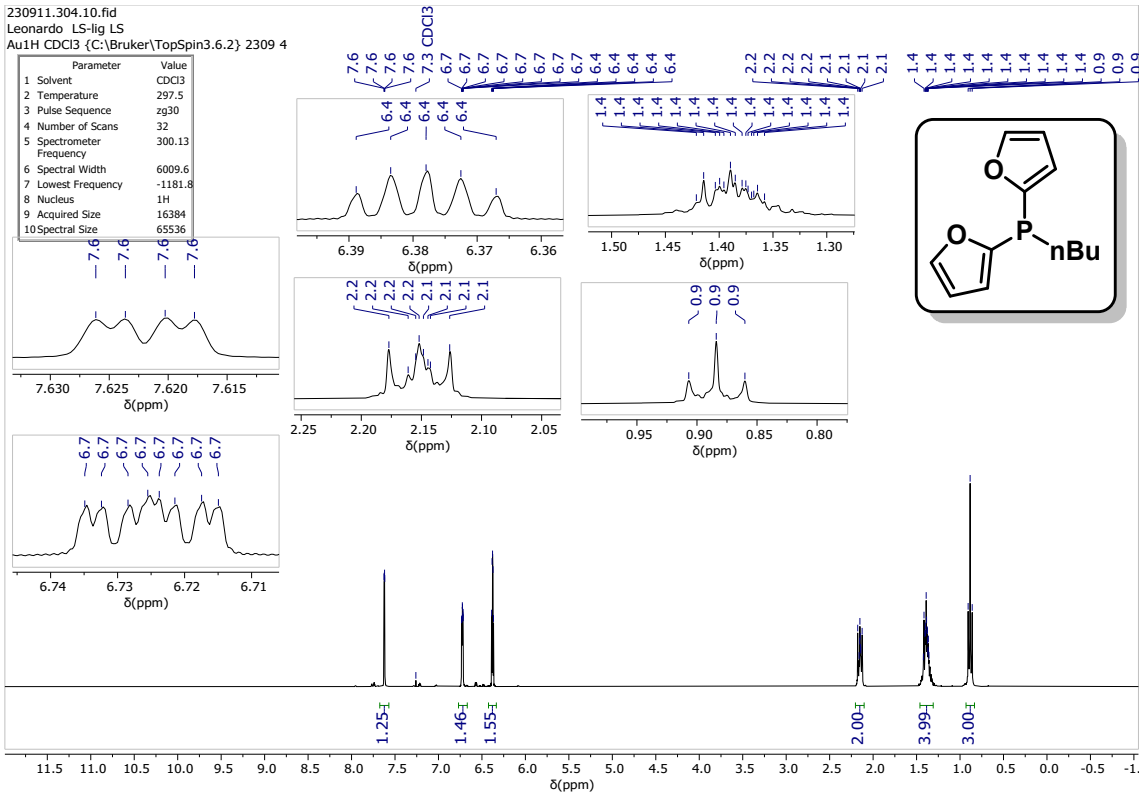


Figure S23: ^{1}H NMR of compound **(L14)**.

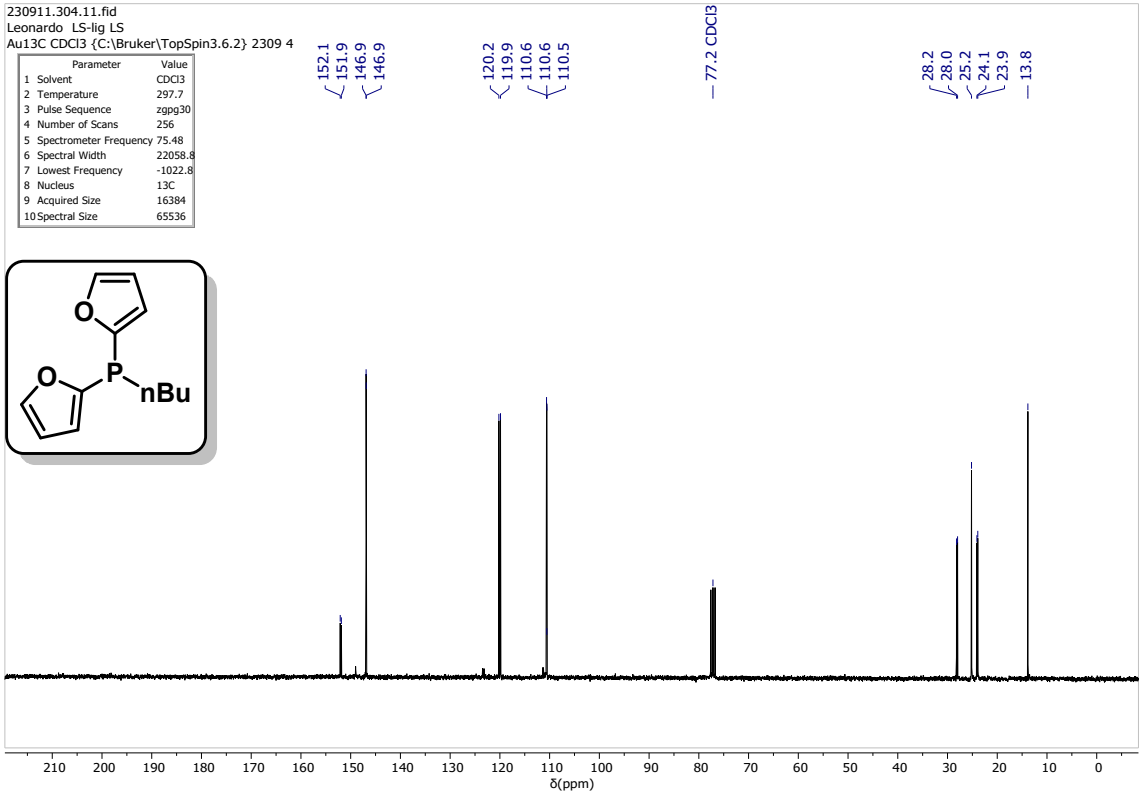


Figure S24: ^{13}C NMR of compound **(L14)**.

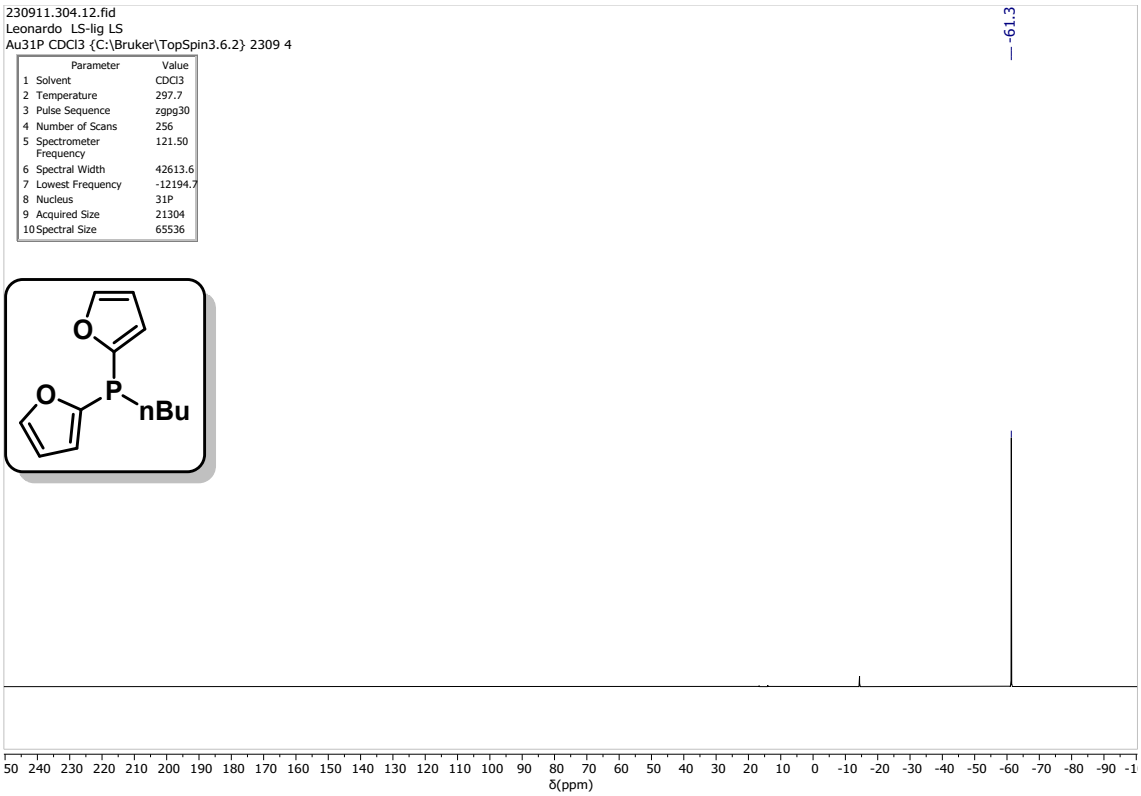


Figure S25: ^{31}P NMR of compound **(L14)**.

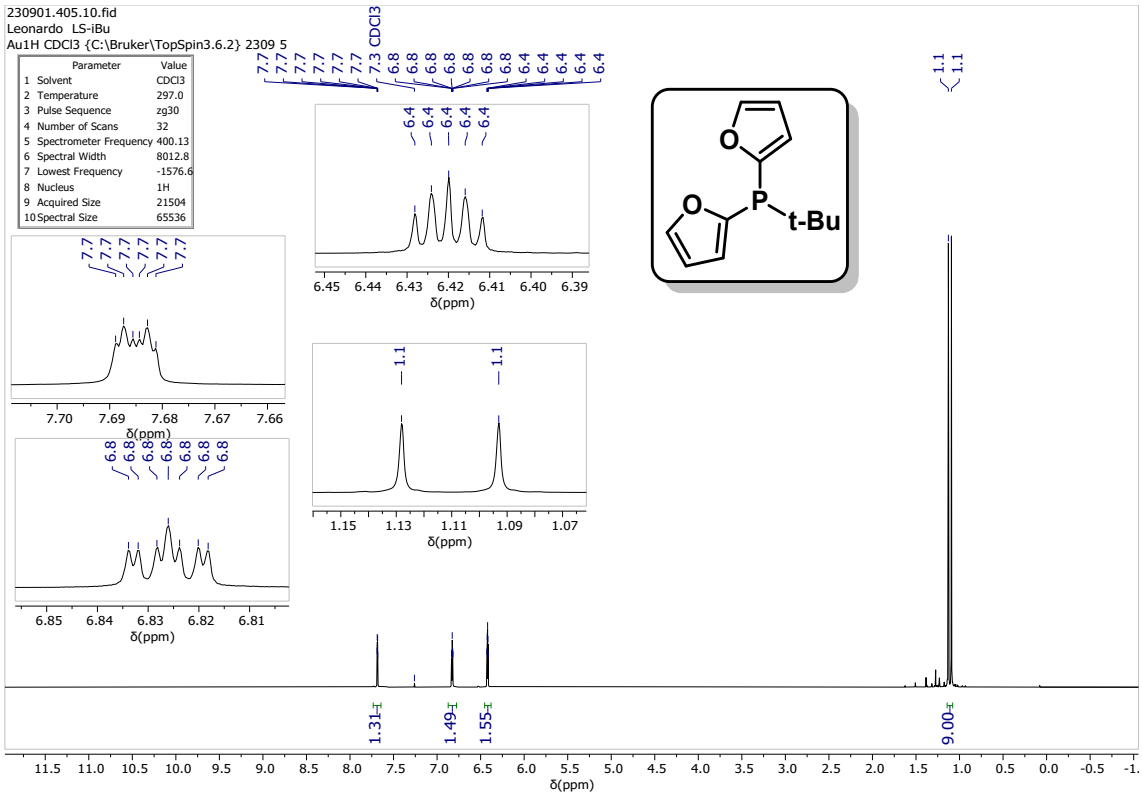


Figure S26: ^{1}H NMR of compound **(L15)**.

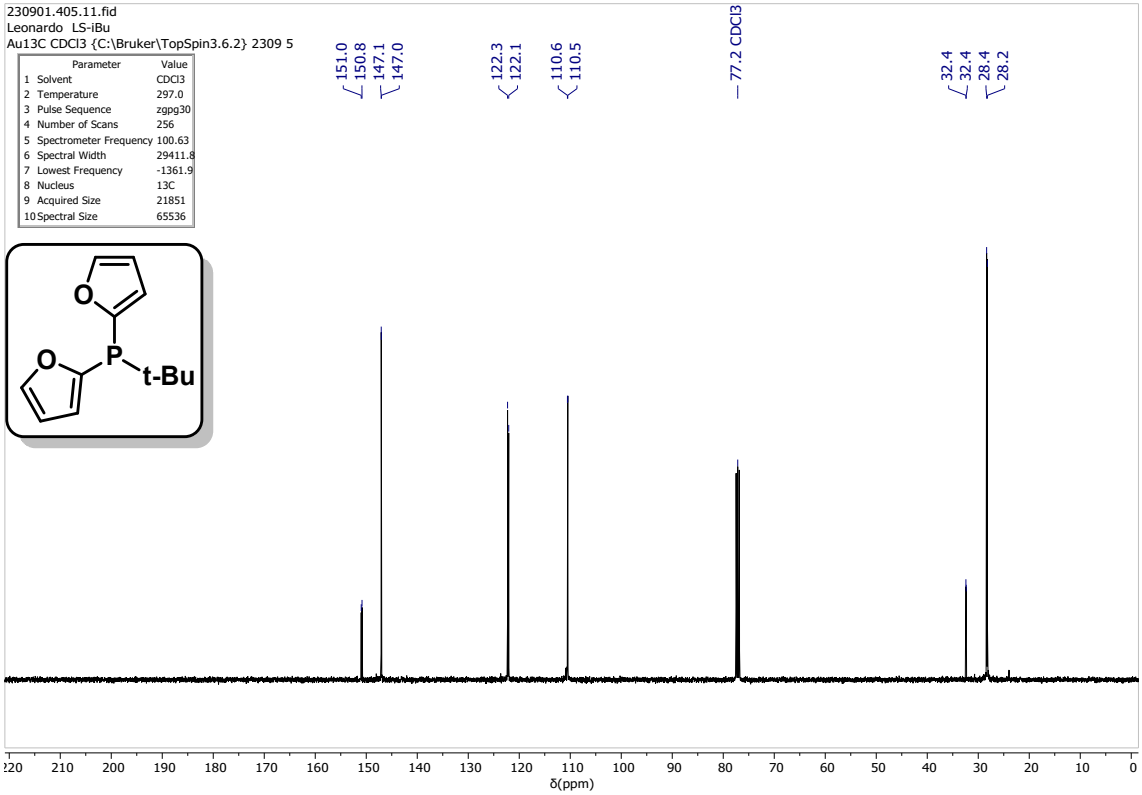


Figure S27: ^{13}C NMR of compound **(L15)**.

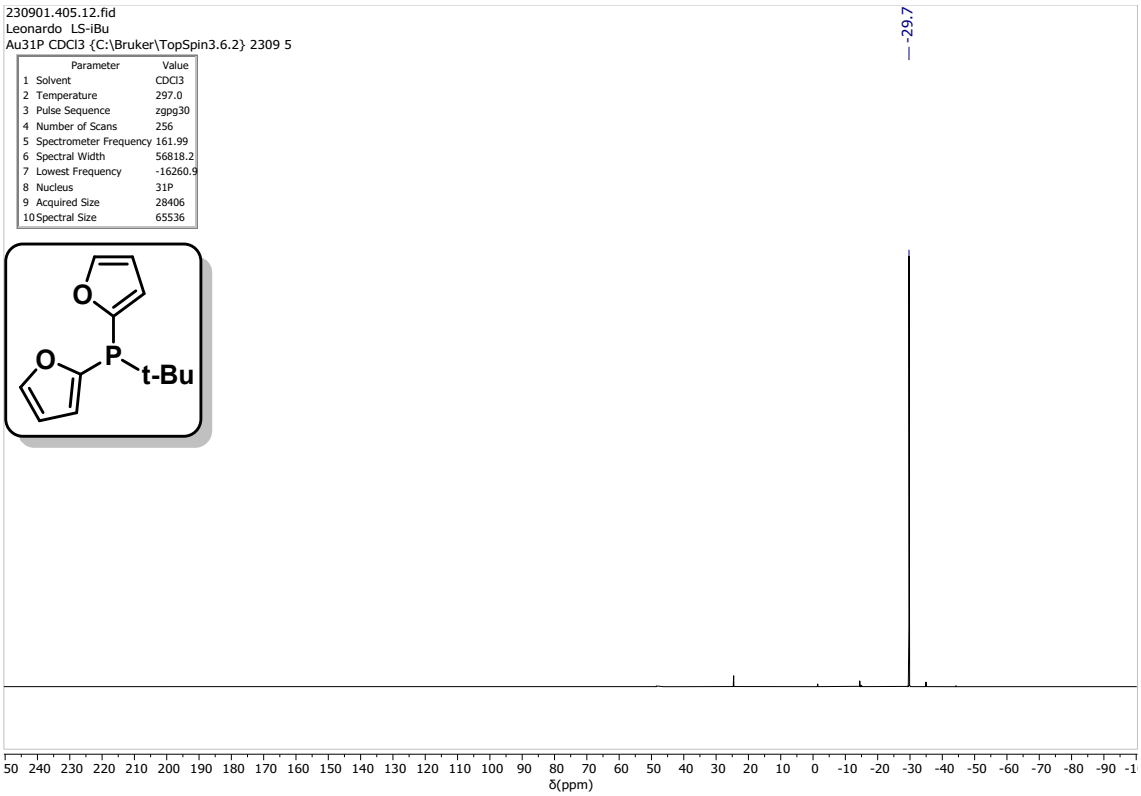


Figure S28: ^{31}P NMR of compound **(L15)**.

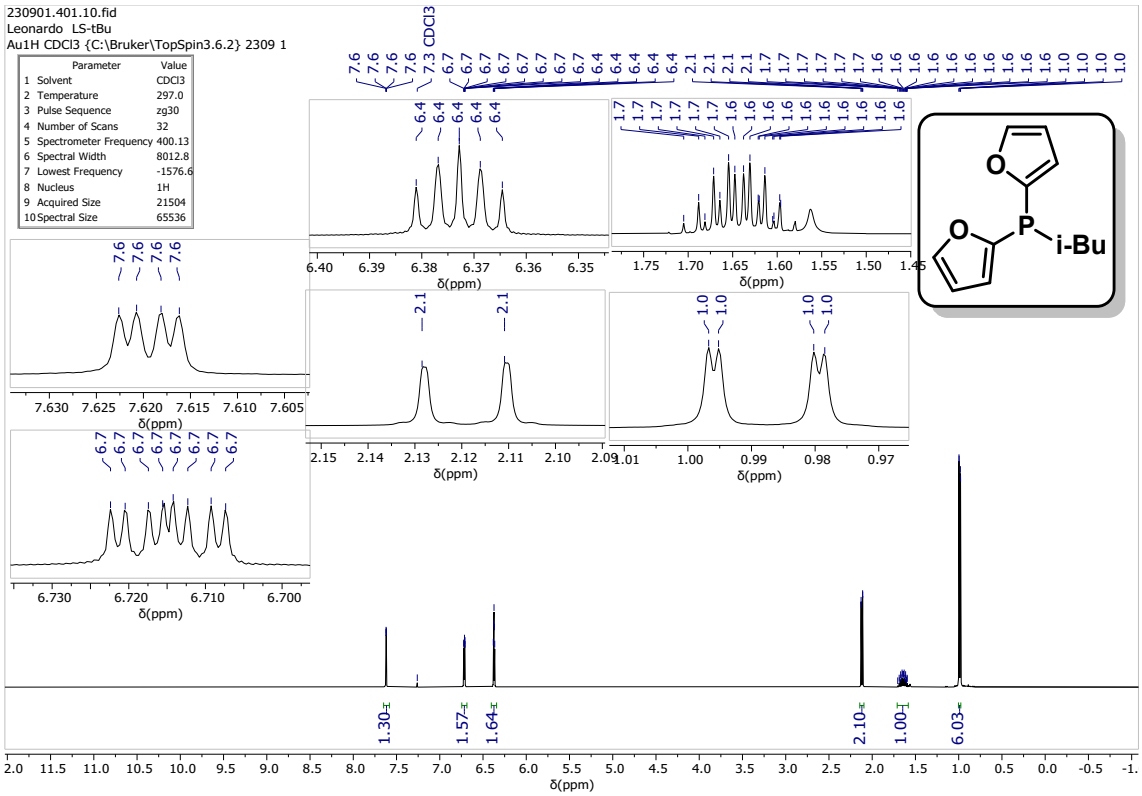


Figure S29: ^{1}H NMR of compound **(L10)**.

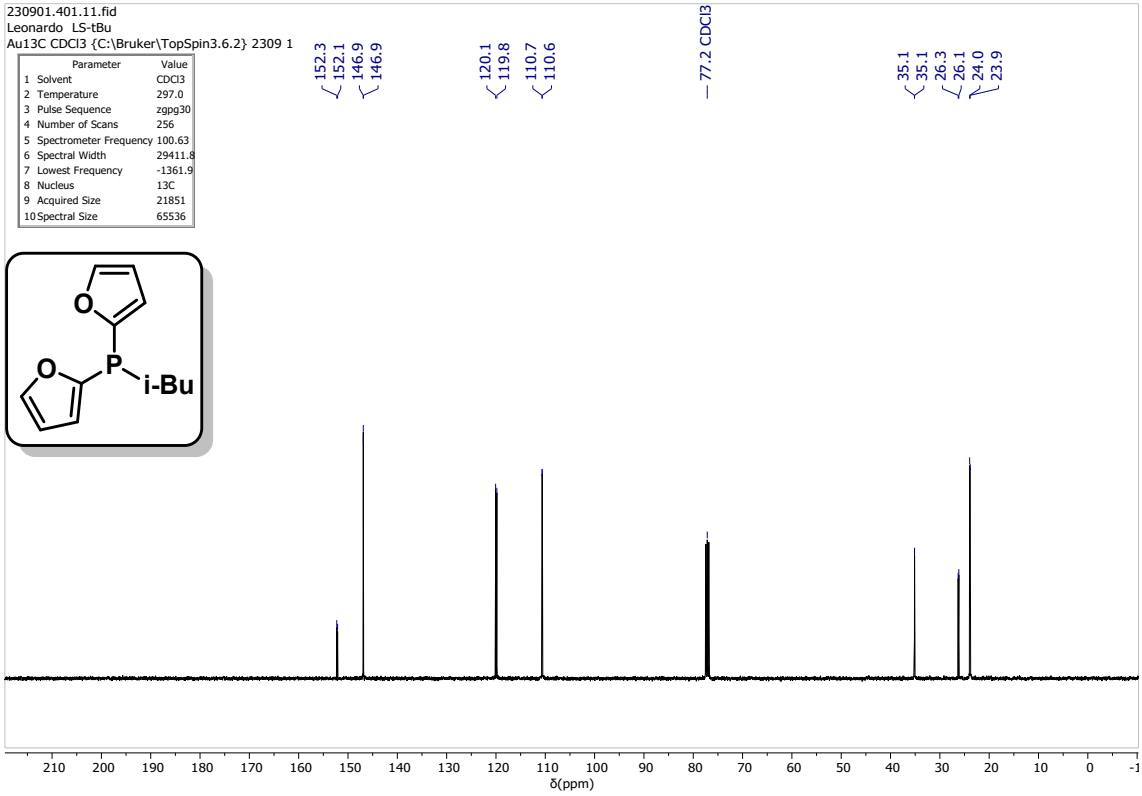


Figure S30: ^{13}C NMR of compound **(L10)**.

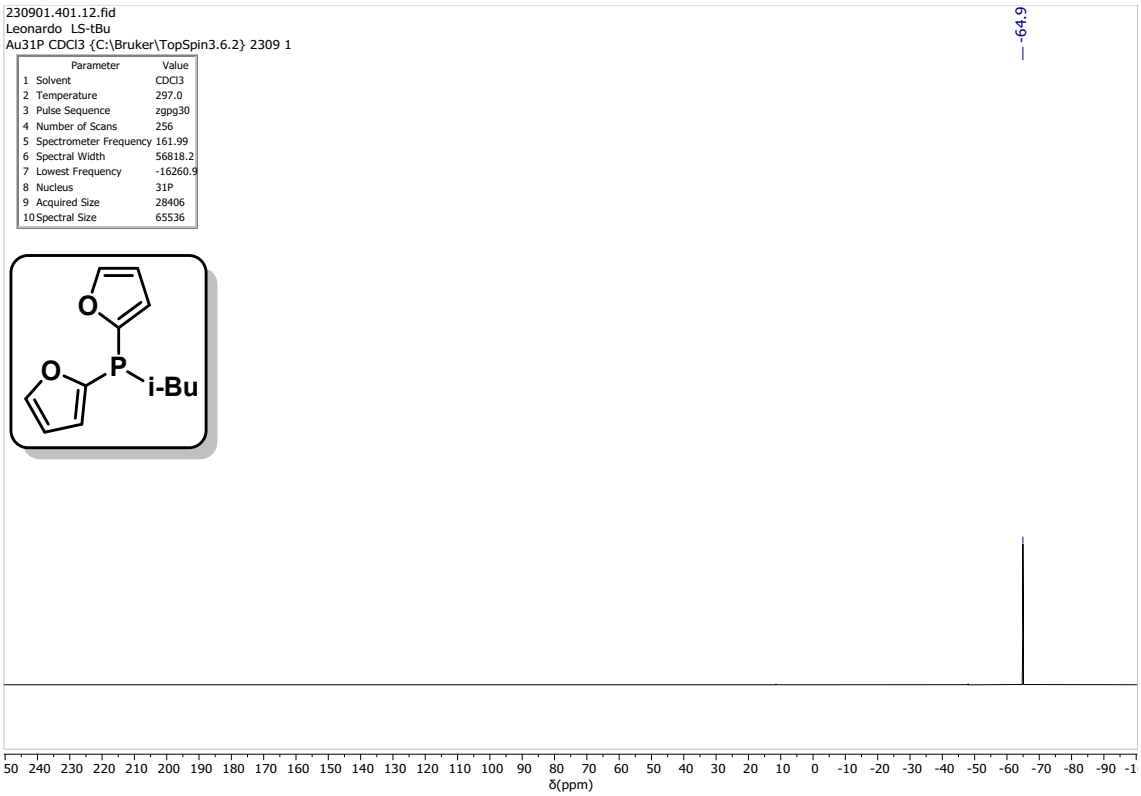


Figure S31: ^{31}P NMR of compound **(L10)**.

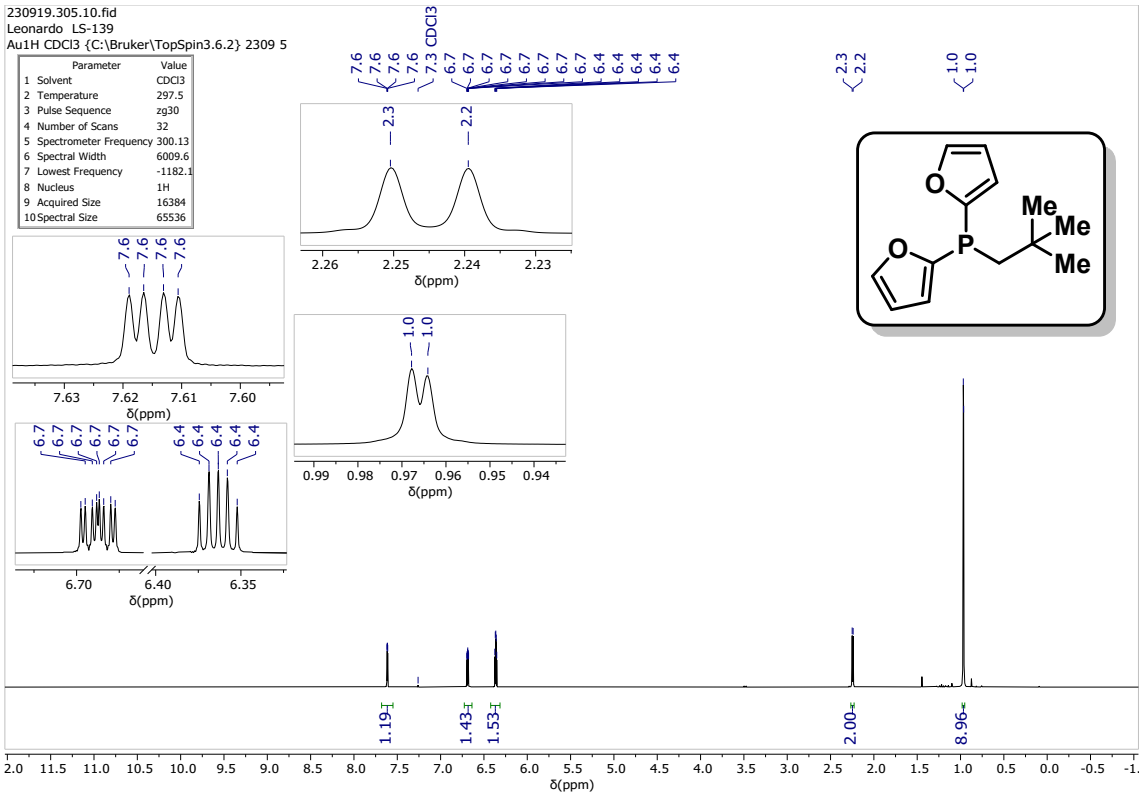


Figure S32: ^{1}H NMR of compound **(L16)**.

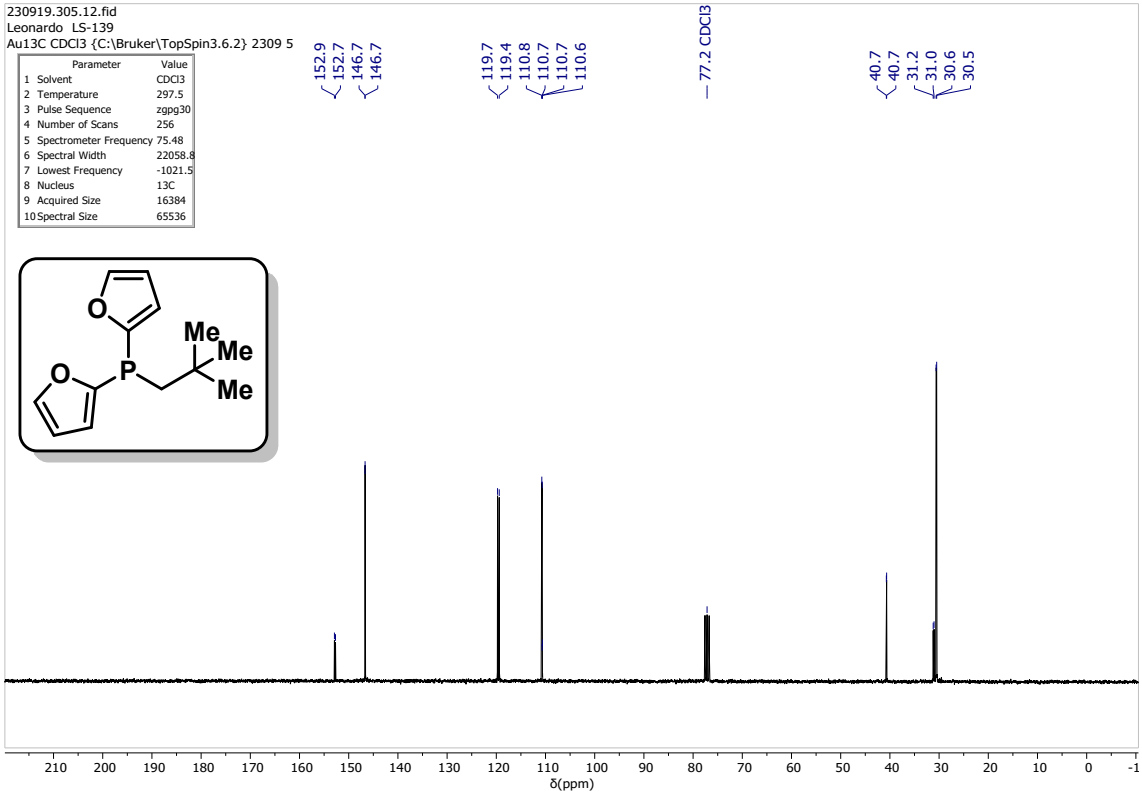


Figure S33: ^{13}C NMR of compound **(L16)**.

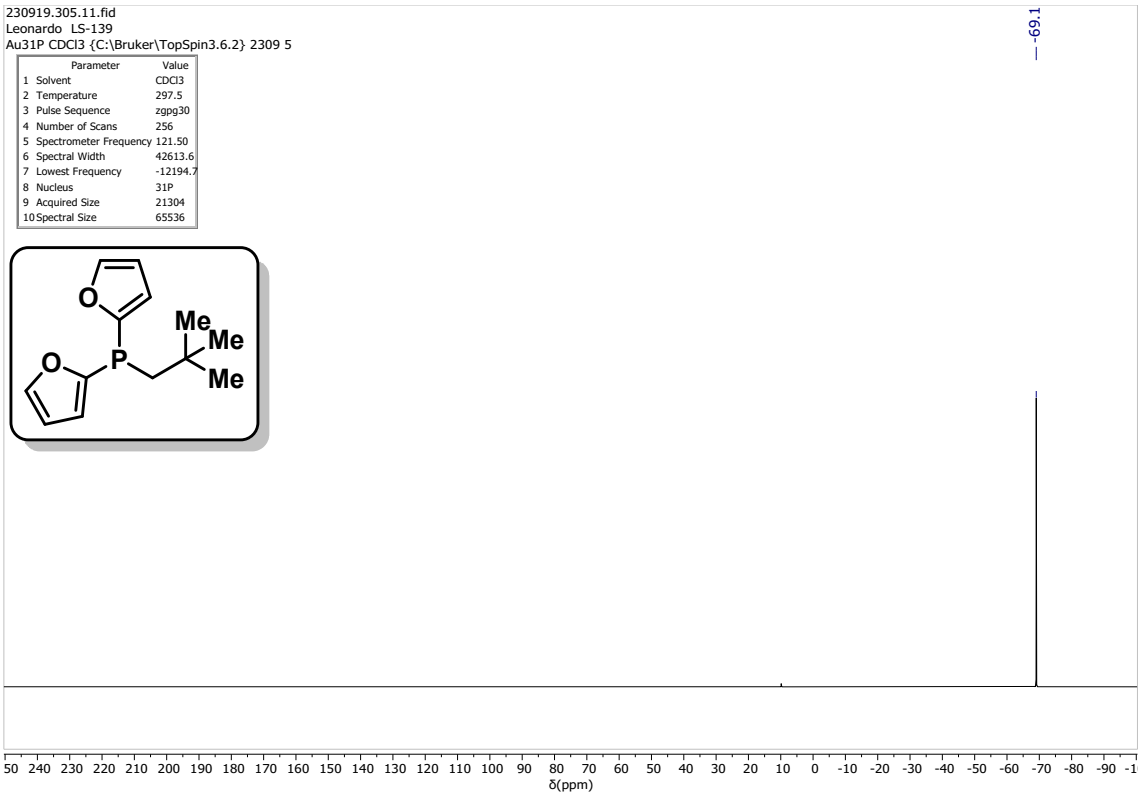


Figure S34: ^{31}P NMR of compound **(L16)**.

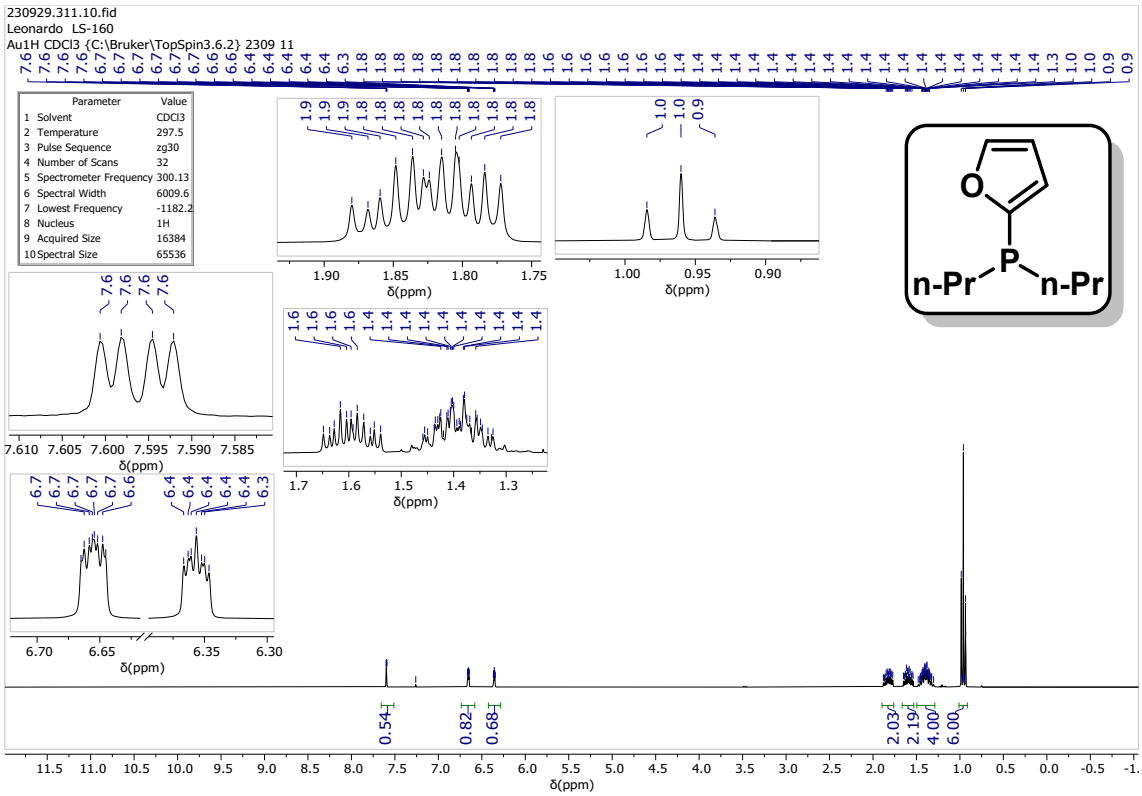


Figure S35: ^{1}H NMR of compound **(L17)**.

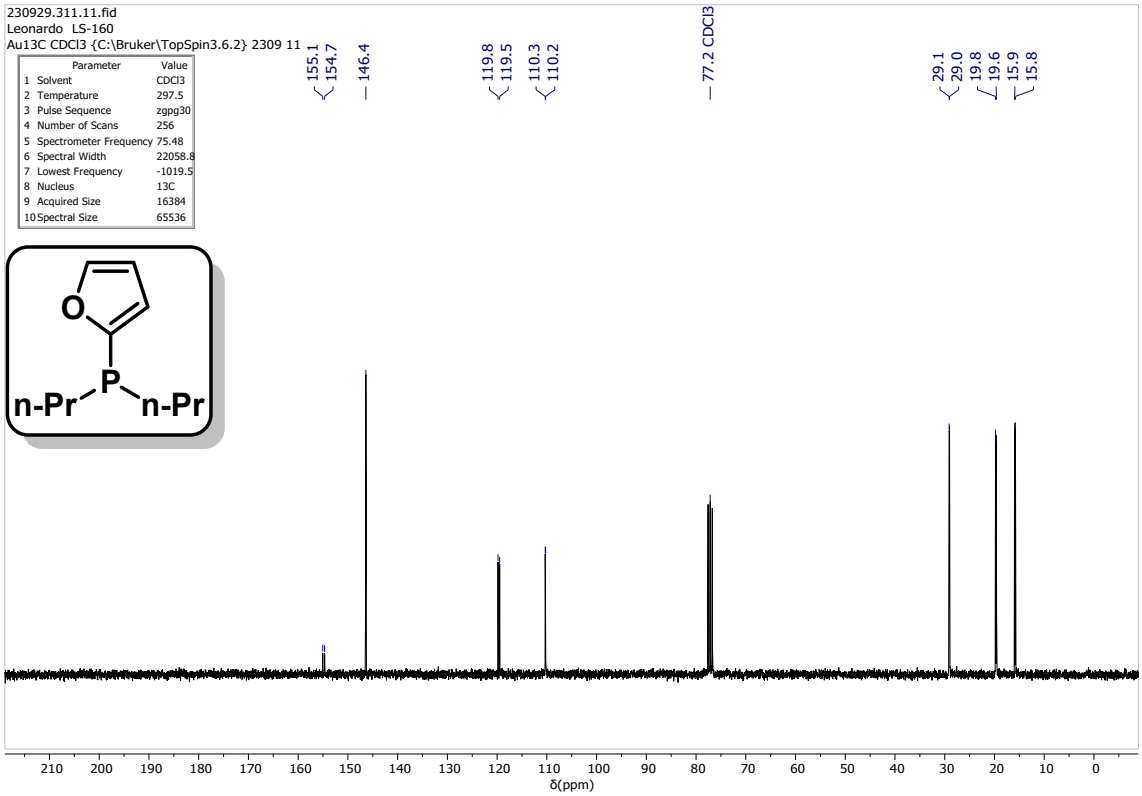


Figure S36: ^{13}C NMR of compound **(L17)**.

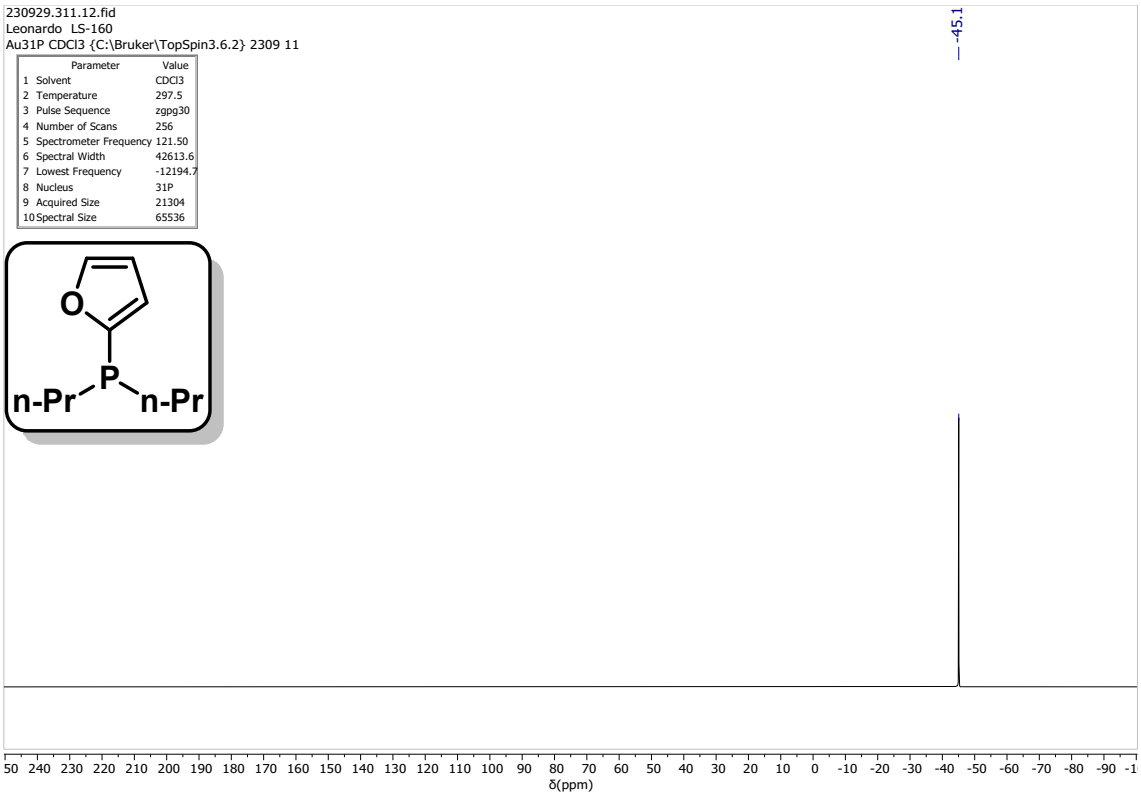


Figure S37: ^{31}P NMR of compound **(L17)**.

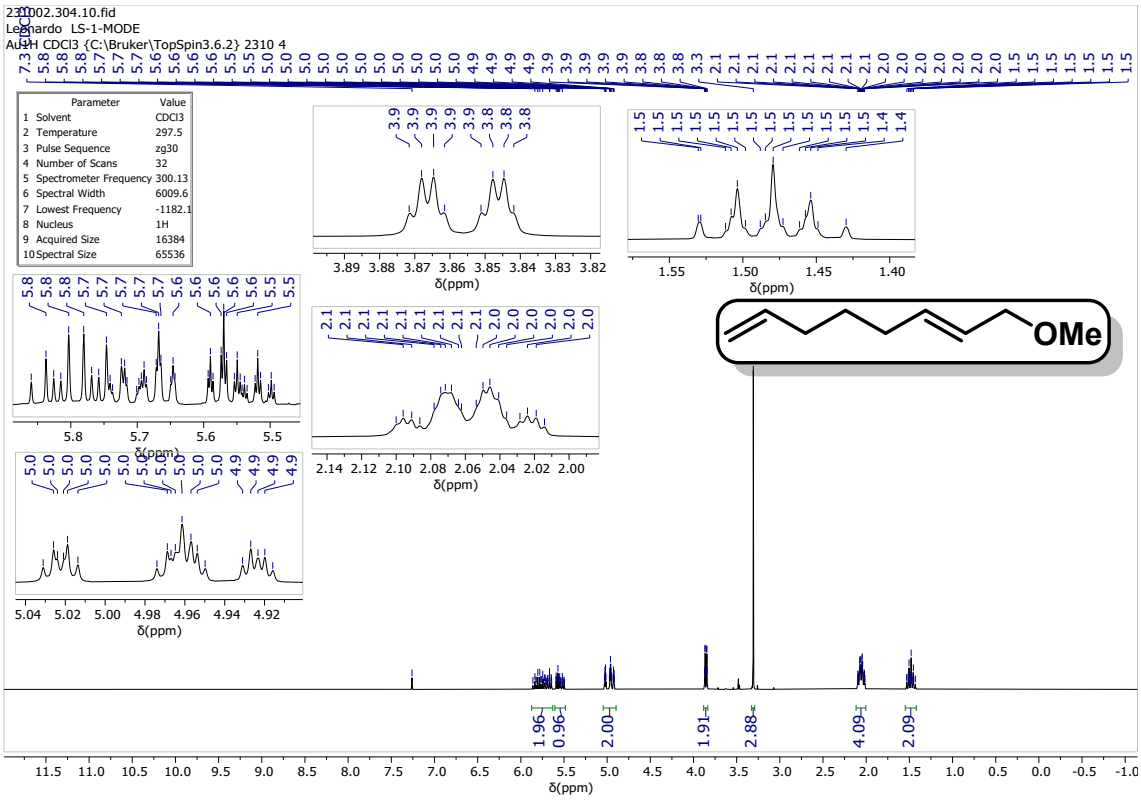


Figure S38: ^{1}H NMR of compound **(2)**.

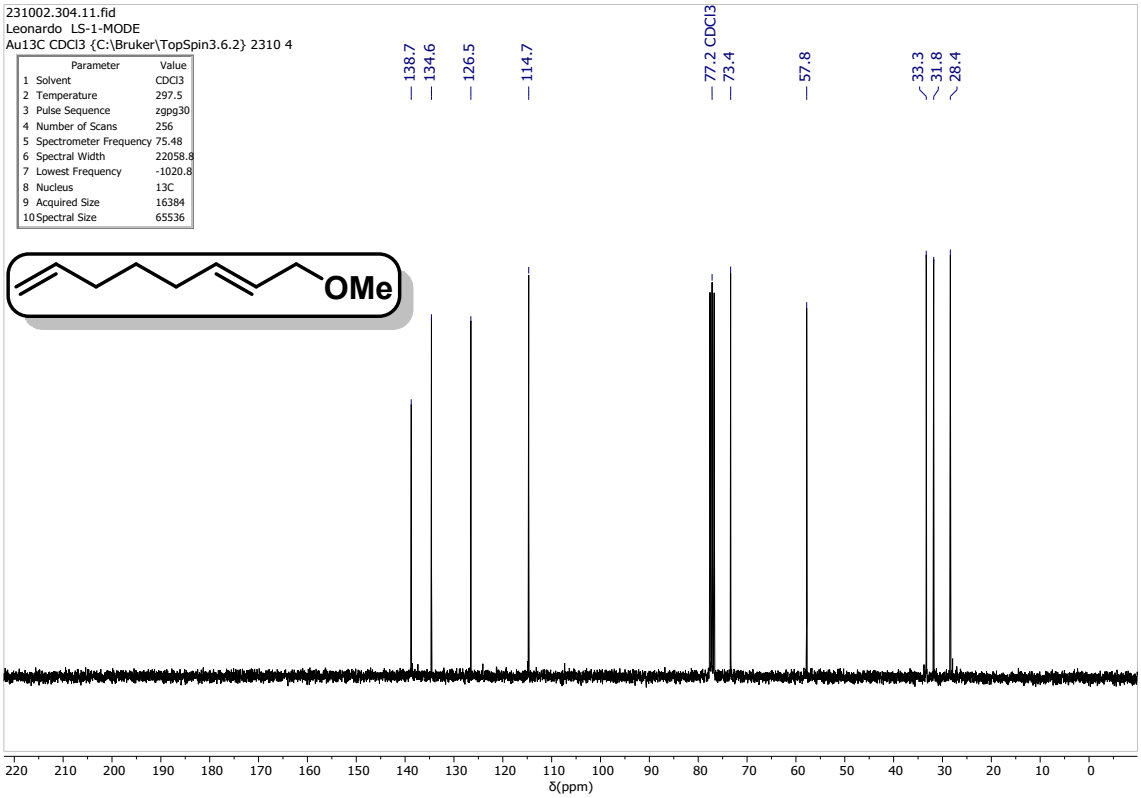


Figure S39: ^{13}C NMR of compound **(2)**.

9. Control experiments

Decomposition experiments:

The first NMR (Figure **40**) was recorded right after the synthesis and purification of the ligand **L11**.

The second NMR (Figure **41**) was recorded after the ligand **L11** was kept on the bench at room temperature under air for one night.

The third NMR (Figure **42**) was recorded after the ligand **L11** was kept on the bench at room temperature under air for one week.

The fourth NMR (Figure **43**) was recorded right after the oxidation of the ligand **L11**.

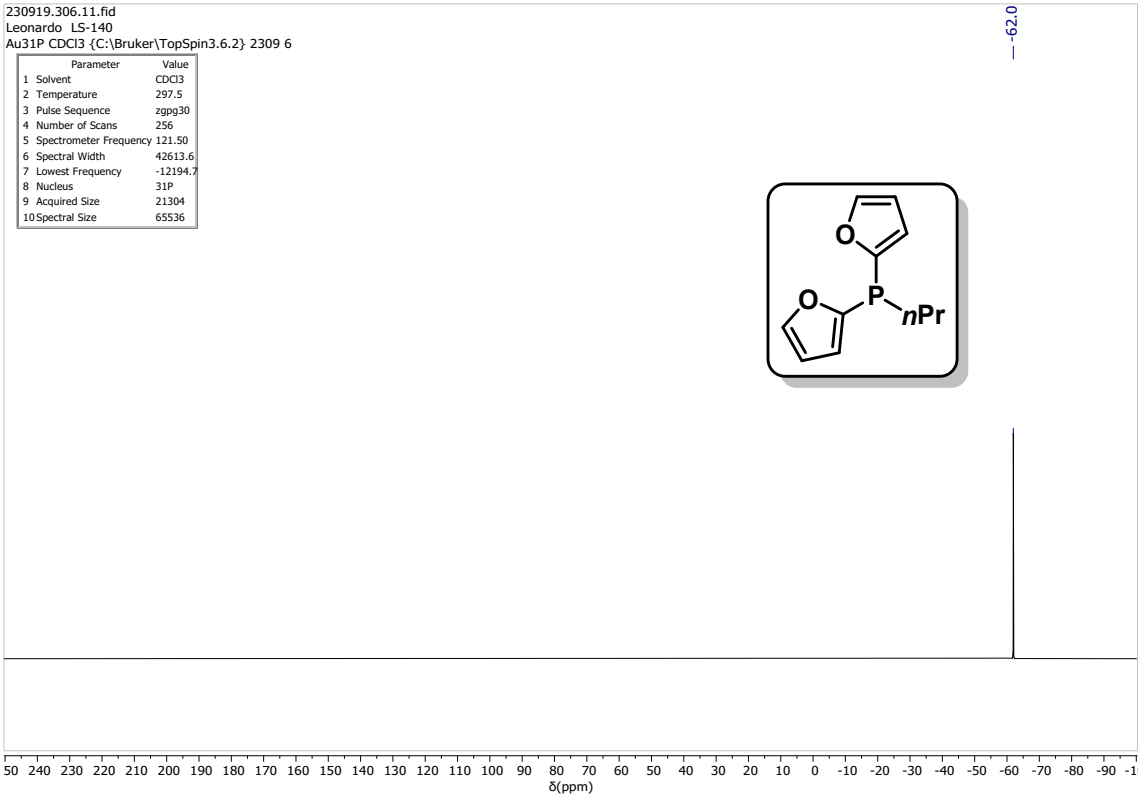


Figure S40: ^{31}P NMR of compound **(L12)**.

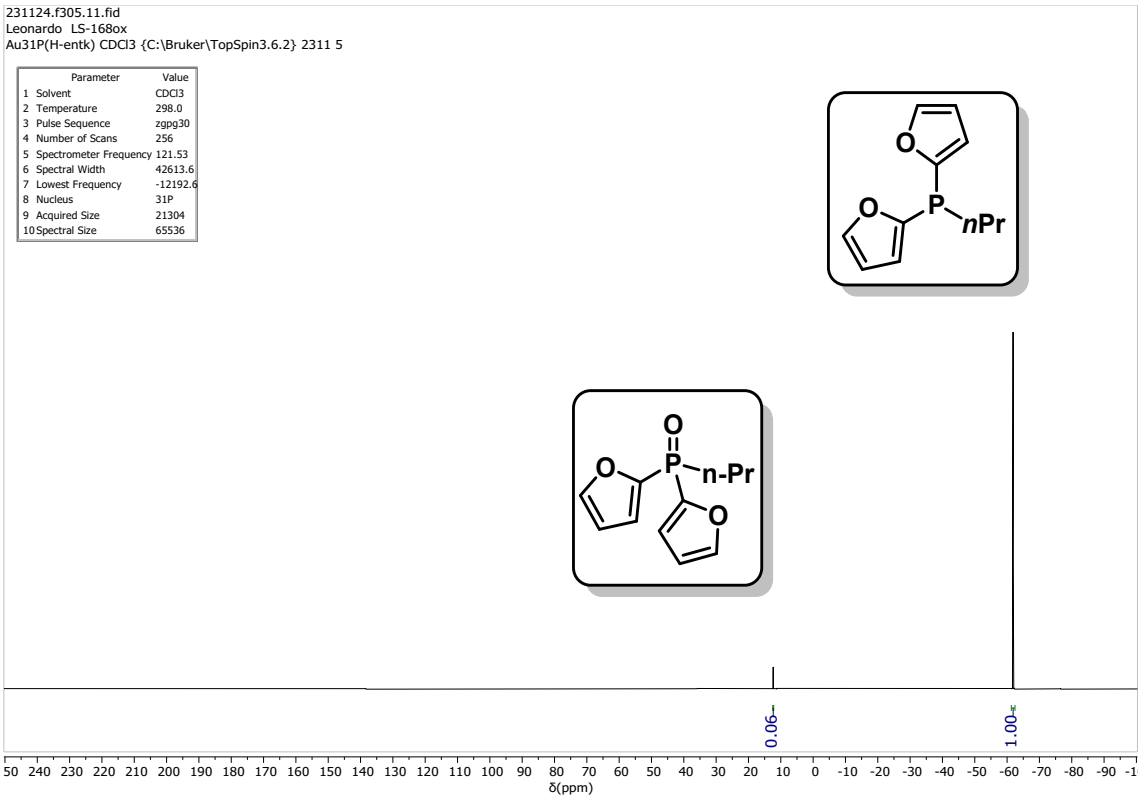


Figure S41: ^{31}P NMR of compound **L12** and **L18**.

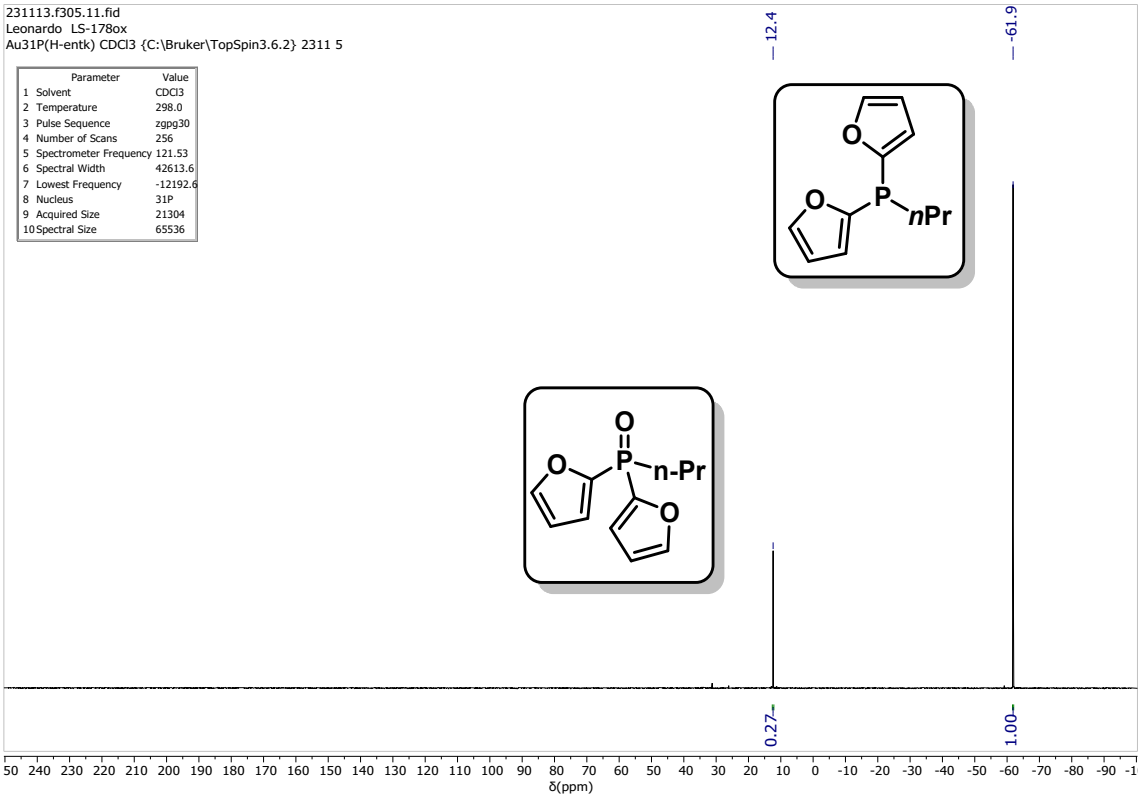


Figure S42: ^{31}P NMR of compound **L12** and **L18**.

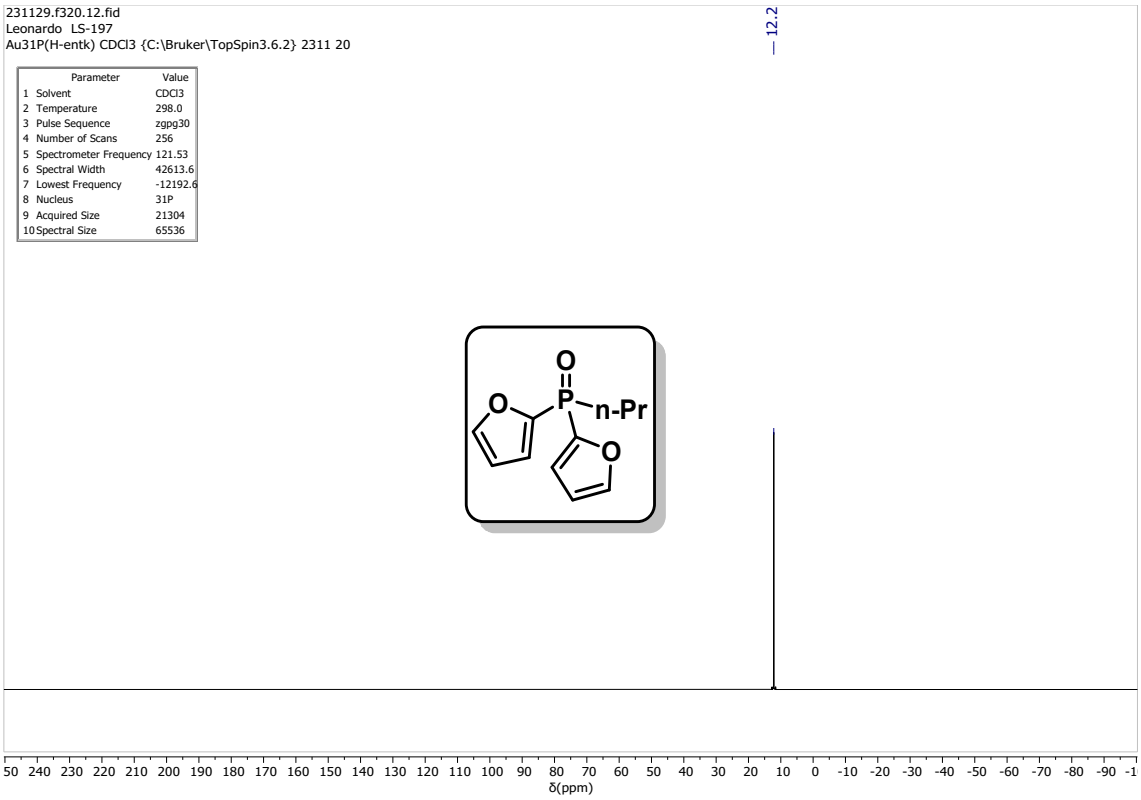


Figure S43: ^{31}P NMR of compound **L18**.

References

[1] Z. Jian, P. Wucher, S. Mecking, *Organometallics* **2014**, *33*, 2879–2888.

[2] C. Laye, J. Lusseau, F. Robert, Y. Landais, *Adv. Synth. Catal.* **2021**, *363*, 3035–3043.