# Supporting Information

## Controlled di-lithiation enabled synthesis of phosphine-sulfonamide ligands and implications in ethylene oligomerization

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# 1. Experimental Section

## 1.1. General methods and materials

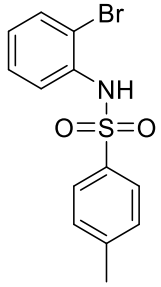
Unless noted otherwise, all manipulations were carried out under an inert atmosphere using standard Schlenk line techniques or glove box. Hexane and THF were distilled from sodium/benzophenone under argon atmosphere. DMSO, pyridine and methylene chloride were distilled from calcium-hydride and stored on activated molecular sieves. Other chemicals like [Pd(COD)MeCl], [Pd(TMEDA)$Me_2$] were synthesized by following known procedures.[1] NMR was recorded on Bruker 400 MHz, and 500 MHz instruments. Chemical shifts are referenced to external reference TMS ($^1$H and $^{13}$C). Coupling constants are given as absolute values. Multiplicities are given as follows s: singlet, d: doublet, t: triplet, m: multiplet. Mass spectra were recorded on Thermo scientific Q-Exactive mass spectrometer, the column specification is Hypersil gold C18 column 150 x 4.6 mm diameter 8 um particle size mobile phase used is 90% methanol + 10 % water + 0.1 % formic acid.IR spectra were recorded on Bruker ALPHA spectrometer. C, H and N analyses were carried out using PerkinElmer 2400 instrument. IR spectra were recorded on Bruker VERTEX 80 spectrophotometer. The samples were prepared as Nujol mull. GPC molecular weights were determined by using Viscoteck GPC, using VE 1122 pump equipped with Viscotek VE 3580 RI detector and Viscotek VE 3210 UV/Vis detector against polystyrene standard.

X-ray diffraction measurement for two ligands **L1A**, **L1B** and three Pd complexes **C1**, **C2**, and **C3**was carried out on a Bruker D8 VENTURE Kappa Duo PHOTON II CPAD diffractometer equipped with Incoatech multilayer mirrors optics. The intensity measurements were carried out with Mo micro-focus sealed tube diffraction source ($MoK_\alpha$= 0.71073 Å) at 100(2) K temperature. The X-ray generator was operated at 50 kV and 1.4 mA. A preliminary set of cell constants and an orientation matrix were calculated from three sets of 36 frames.Data were collected with $\omega$and$\varphi$scan width of 0.5° at different settings of $\varphi$, $\omega$ and $2\theta$keeping the sample-to-detector distance fixed at 5.00 cm. The X-ray data collection was monitored by the APEX3 program (Bruker, 2016).[2] All the data were corrected for Lorentzian, polarization, and absorption effects using SAINT and

SADABS programs (Bruker, 2016). Using the APEX3 (Bruker) program suite, the structure was solved with the ShelXS-97 (Sheldrick, 2008)[3] structure solution program, using direct methods. The model was refined with a version of ShelXL-2013 (Sheldrick, 2015)[4]using Least Squares minimization. All the hydrogen atoms were placed in a geometrically idealized position and constrained to ride on its parent atoms. An *ORTEP* III[5] view of the compound was drawn with either 30% or 50% probability displacement ellipsoids, and H atoms are shown as small spheres of arbitrary radii. For compound **C2**,PLATON/SQUEEZE was used to correct the diffraction data for the contribution from disordered lattice solvent molecules. The solvent-accessible void volume per unit cell was 144 $A^3$ (5%) and Electron Count/unit Cell was 38 $e/A^{-3}$, estimated by PLATON.

## 2. Synthesis of ligands

### 2.1. Synthesis of *N*-(2-bromophenyl)-4-methylbenzenesulfonamide (1):




4-methylbenzenesulfonyl chloride (3.65 gm, 19.1 mmol) was dissolved in 50 mL DCM and the flask was maintained at 0 ºC. In another round bottom flask, 2-Bromoaniline (1.97 mL, 17.4 mmol) was dissolved in 50 mL DCM and pyridine (2.81 mL, 34.8 mmol) was syringed. The solution of 2-Bromoaniline and pyridine was added drop wise to the solution of 4-methylbenzenesulfonyl chloride at 0 ºC. Reaction mixture turns brown (from colorless), which was stirred for 18 hours at room temperature. 1N hydrochloric acid (150 mL) was added and organic layer was separated. Organic layer was washed with distilled water (150 mL) and then washed with brine solution (150 mL). DCM was evaporated and the product was purified by using column chromatography (DCM:Petroleum ether 30:70) in 81 % yield.

**$^1$H-NMR** (200 MHz in $CDCl_3$):δ = 7.64 (m, 3H, Ar-H), 7.40 (m, 1H, Ar-H), 7.26 (m, 1H, Ar-H), 7.21 (d, 2H, Ar-H, *J* = 8.3 Hz), 6.99 (s, 1H, NH), 6.96 (m, 1H, Ar-H), 2.36 (s, 3H, *p*-Me). **$^{13}$C-NMR**(125 MHz in $CDCl_3$):δ = 144.2 (Cq), 135.7 (Cq), 134.6 (Cq), 132.5, 129.6, 128.5, 127.2, 126.2, 122.5, 115.6 (Cq), 21.5. **IR (Nujol)** $cm^{-1}$= 1377 and 1276 (S=O), 3393

(C–H). **IR (Nujol)** $cm^{-1}$= 1379 and 1159 (S=O), 3294 (C–H). **ESI-MS:** Calculated *m/z* for$[C_{13}H_{13}BrNO_2S]^+$= 325.9850; found *m/z* = 325.9851 $[M+H]^+$.

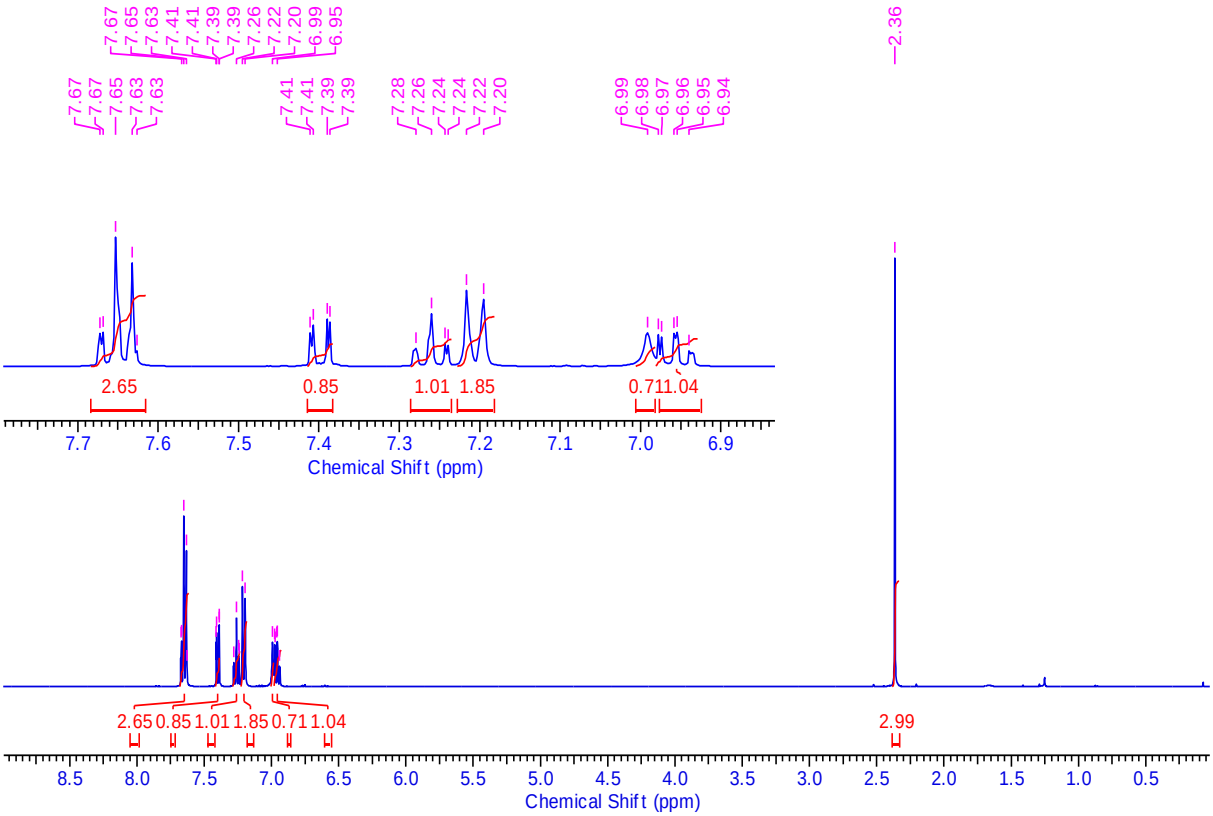



**Figure S1:** $^1$H NMR spectrum of *N*-(2-bromophenyl)-4-methylbenzenesulfonamide (**1**).

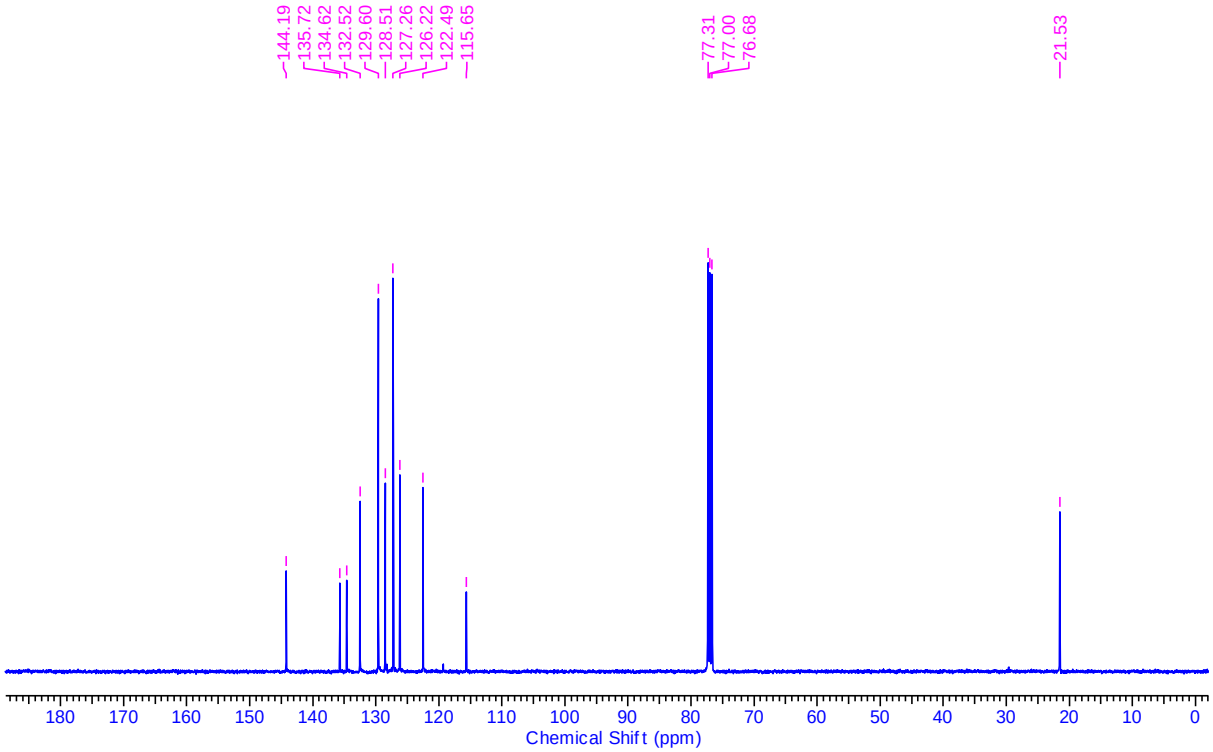



**Figure S2:** $^{13}$C-NMR spectrum of *N*-(2-bromophenyl)-4-methylbenzenesulfonamide (**1**) in $CDCl_3$.

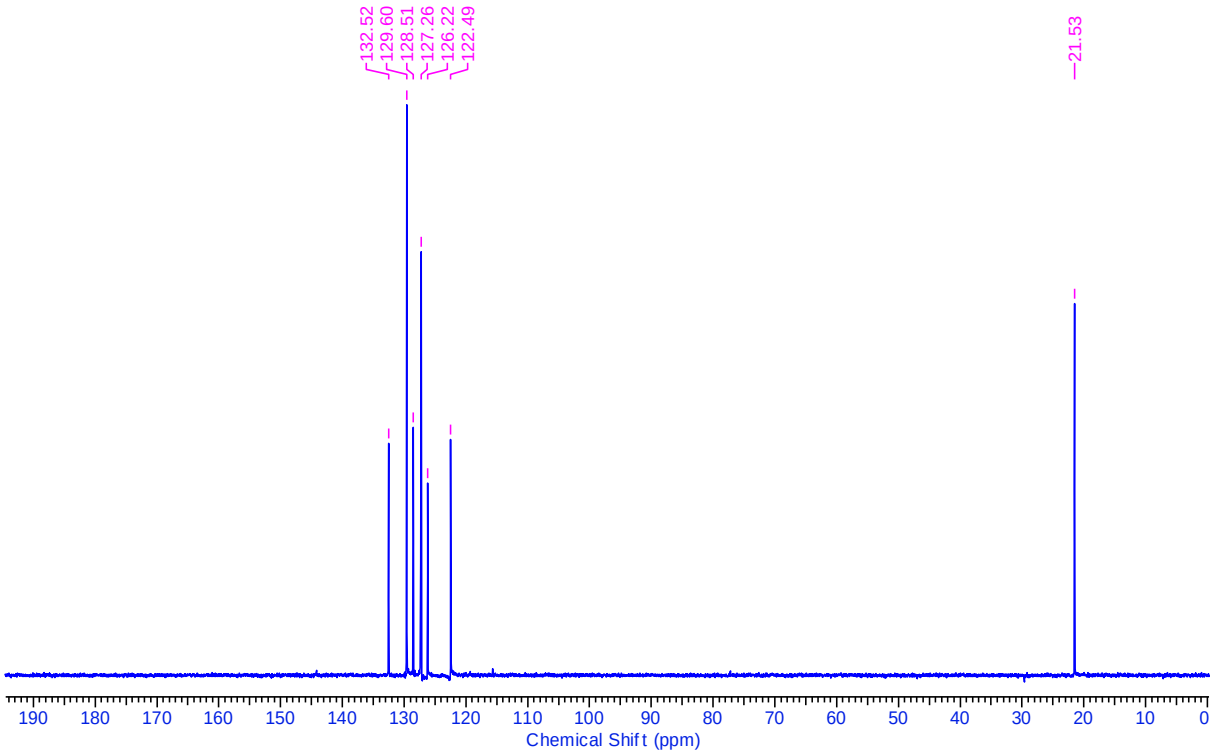



**Figure S3:** DEPT-NMR spectrum of *N*-(2-bromophenyl)-4-methylbenzenesulfonamide (**1**) in $CDCl_3$.

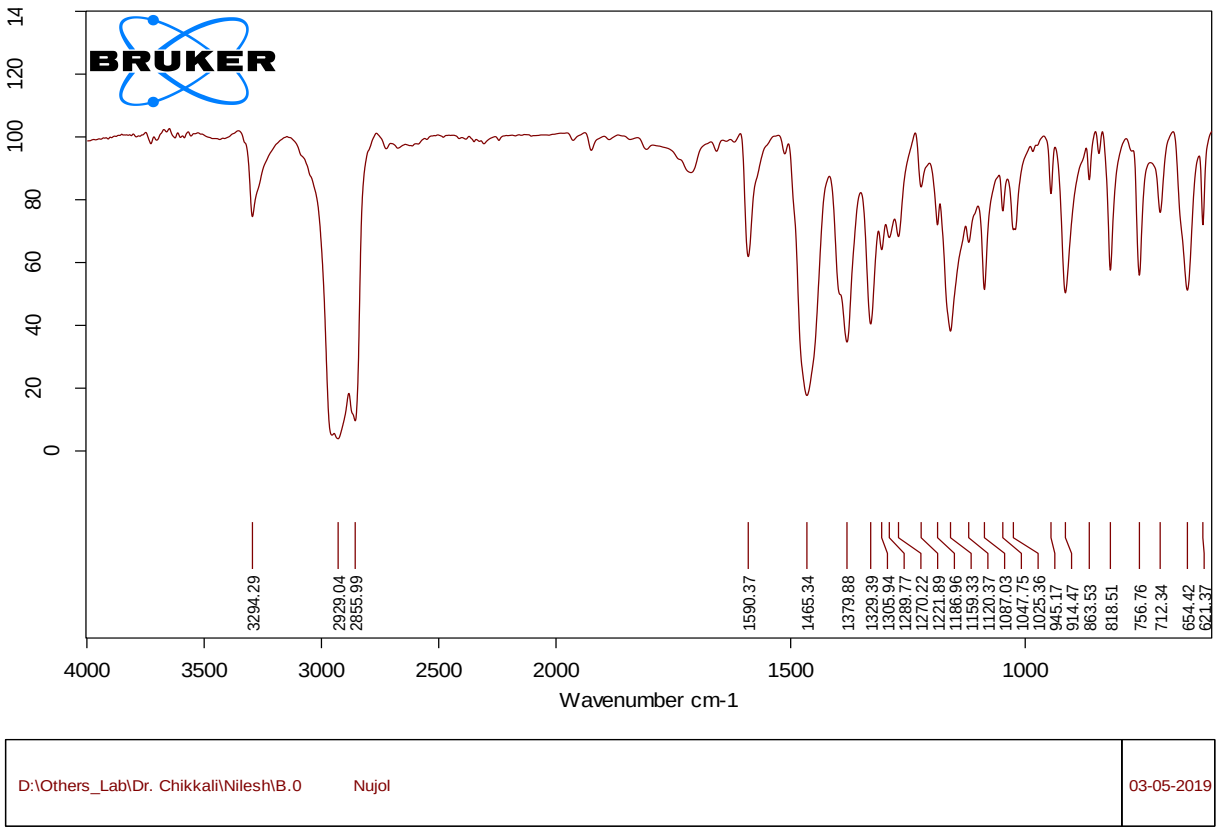



**Figure S4:** IR spectrum of *N*-(2-bromophenyl)-4-methylbenzenesulfonamide (**1**) in Nujol.

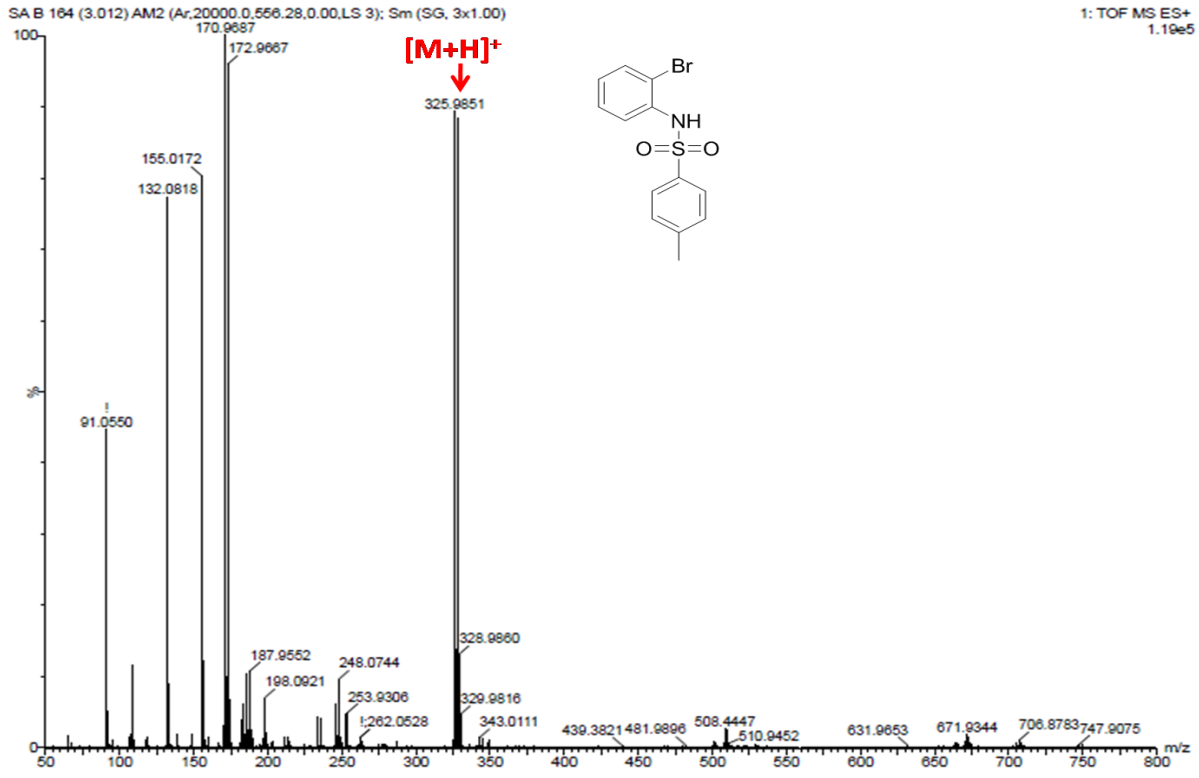
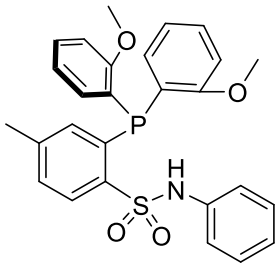



**Figure S5:** ESI-MS spectrum of *N*-(2-bromophenyl)-4-methylbenzenesulfonamide (**1**) in methanol.

## 2.2. Synthesis of 2-(bis(2-methoxyphenyl)phosphanyl)-4-methyl-*N*-phenylbenzenesulfonamide (L2A):



*N*-(2-bromophenyl)-4-methylbenzenesulfonamide (0.5 gm, 1.53 mmol)was dissolved in THF (15 mL) and the reaction mixture was cooled to -41 ºC. *n*-BuLi (2 M) (1.51 mL, 3.03 mmol) was added drop wise with constant stirring. Reaction mixture was stirred for 3 hours (during which the temperature rose to 0 ºC)after which the temperature of the bath was lowered to -41 ºC. Chlorobis(2-methoxyphenyl)phosphane (0.430 gm, 1.53 mmol) in THF (15 mL) was added drop wise to the above lithiated reaction mixture. The resultant content was further stirred overnight (16 hrs) at room temperature. THF was evaporated and the resultant residue was dissolved in DCM (40 mL), followed by addition of degassed water (20 mL). HCl in diethyl ether (2 M) (0.76 mL, 1.53 mmol) was added and the content was stirred for 10 minutes. Organic layer was extracted under argon and was dried on sodium sulfate. DCM was evaporated and crude solid was dried under vacuum for 2 hours. Compound was purified by precipitation in DCM:*n*-pentane at 0 ºC in 80 % isolated yield.

**$^{31}$P NMR** (500 MHz in $CDCl_3$): δ = -30.04.**$^{1}$H NMR** (500 MHz in $CDCl_3$): δ = 8.07 (m, 1H, Ar-H), 7.89 (m, 1H, Ar-H), 7.37 (m, 2H, Ar-H), 7.22- 7.25 (m, 3H, Ar-H/NH) 7.17 (m, 1H, Ar-H), 7.08 (m, 2H, Ar-H), 6.88 (m, 5H, Ar-H), 6.69 (m, 2H, Ar-H), 3.61 (s, 6H, *o*-OMe), 2.20 (s, 3H, *p*-Me).**$^{13}$CNMR** (125 MHz in $CDCl_3$): δ = 160.7,142.6, 137.1, 136.4, 134, 130.5, 128.8, 124.8, 121.8, 121, 0.9, 110.3, 55.4, 21.3, **ESI-MS:** Calculated *m/z* for$[C_{27}H_{27}O_4NPS]^+$= 492.1393 $[M+H]^+$; found *m/z* = 492.1392 $[M+H]^+$.

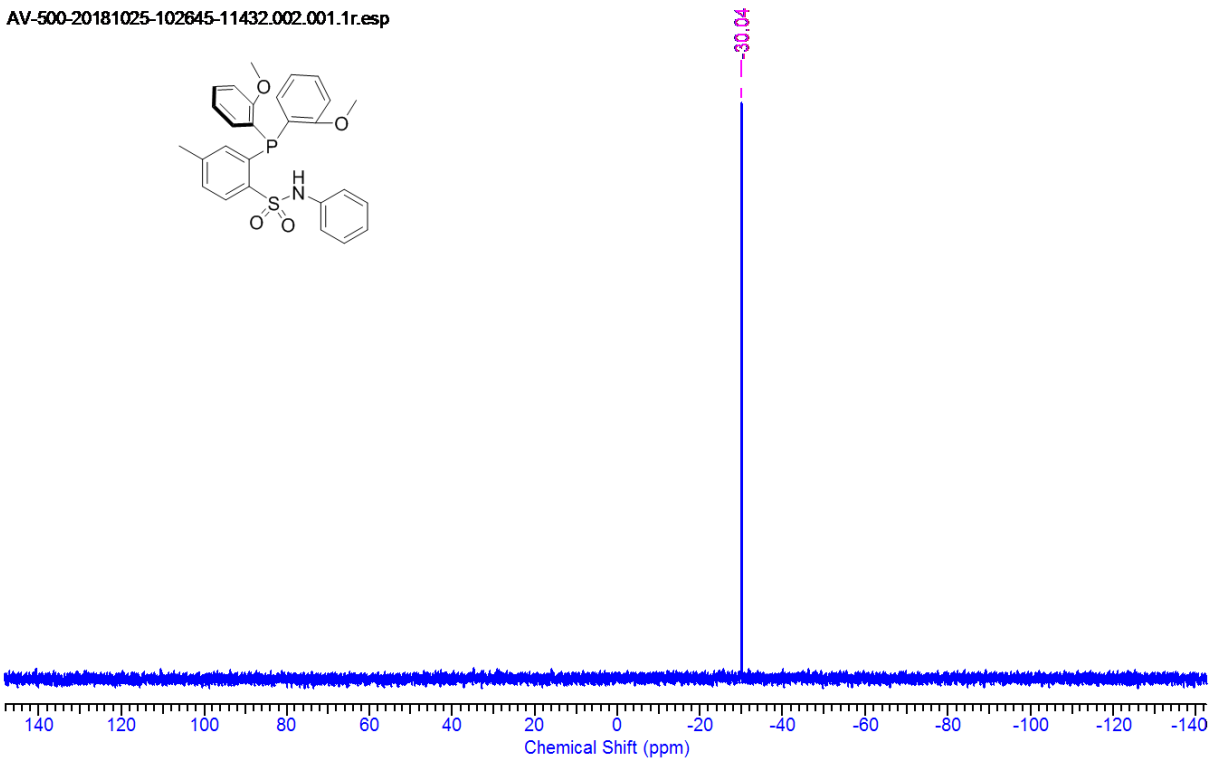



**Figure S6:** $^{31}$PNMR spectrum of ligand 2-(bis(2-methoxyphenyl)phosphaneyl)-4-methyl-*N*-phenylbenzenesulfonamide (**L2A**) in $CDCl_3$.

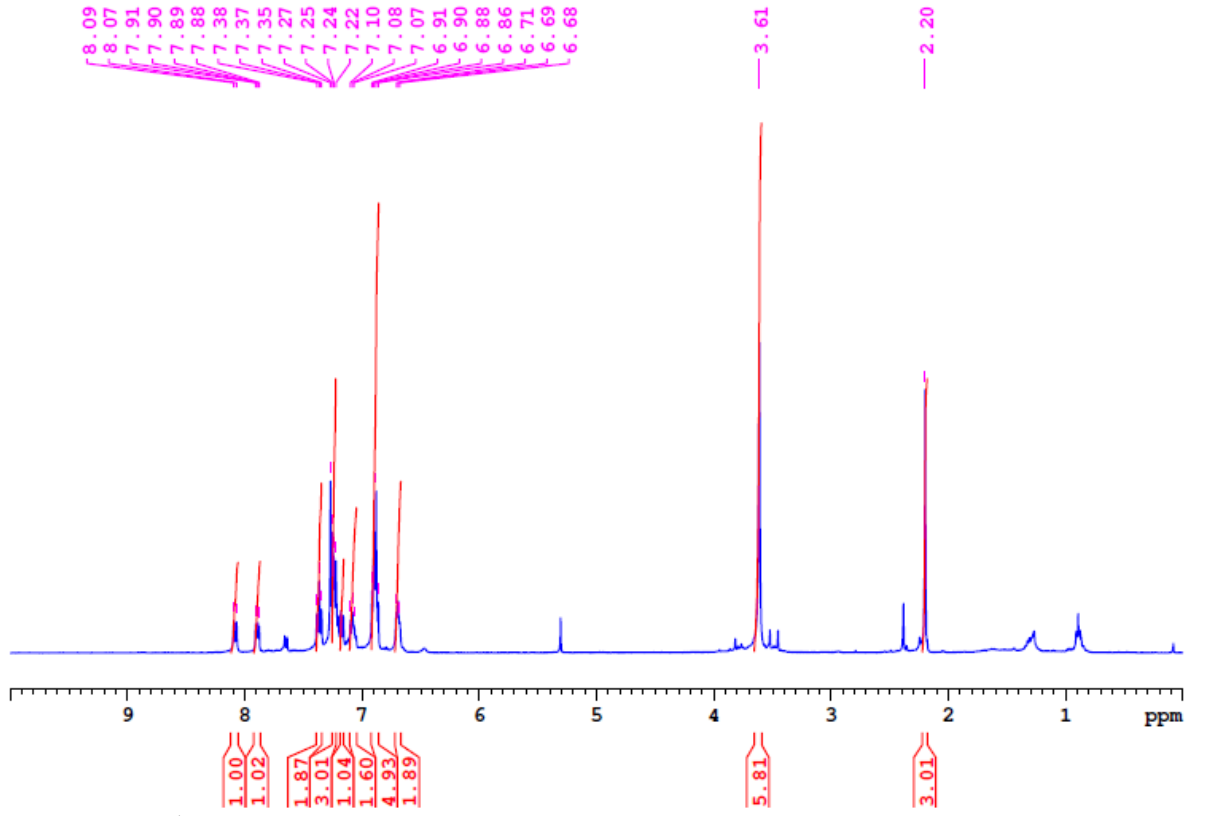



**Figure S7:** $^{1}$H NMR spectrum of ligand 2-(bis(2-methoxyphenyl)phosphaneyl)-4-methyl-*N*-phenylbenzenesulfonamide (**L2A**) in $CDCl_3$.

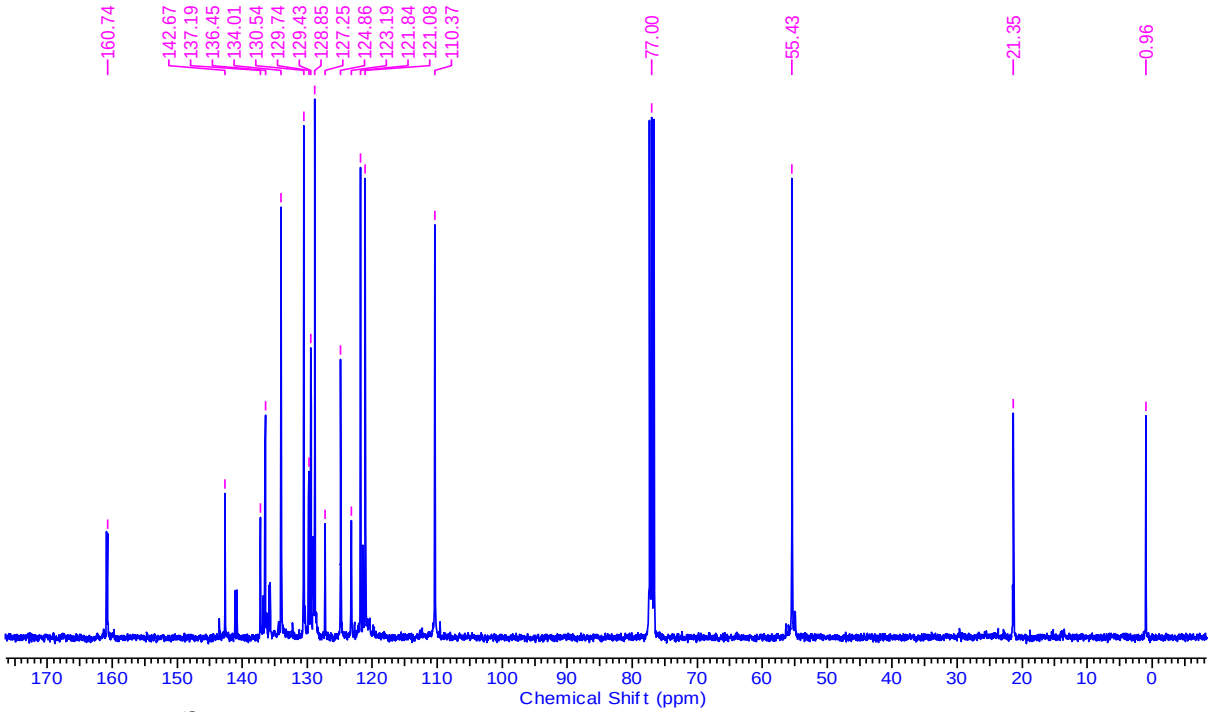



**Figure S8:** $^{13}C$ NMR spectrum of ligand 2-(bis(2-methoxyphenyl)phosphaneyl)-4-methyl-*N*-phenylbenzenesulfonamide (**L2A**) in $CDCl_3$.

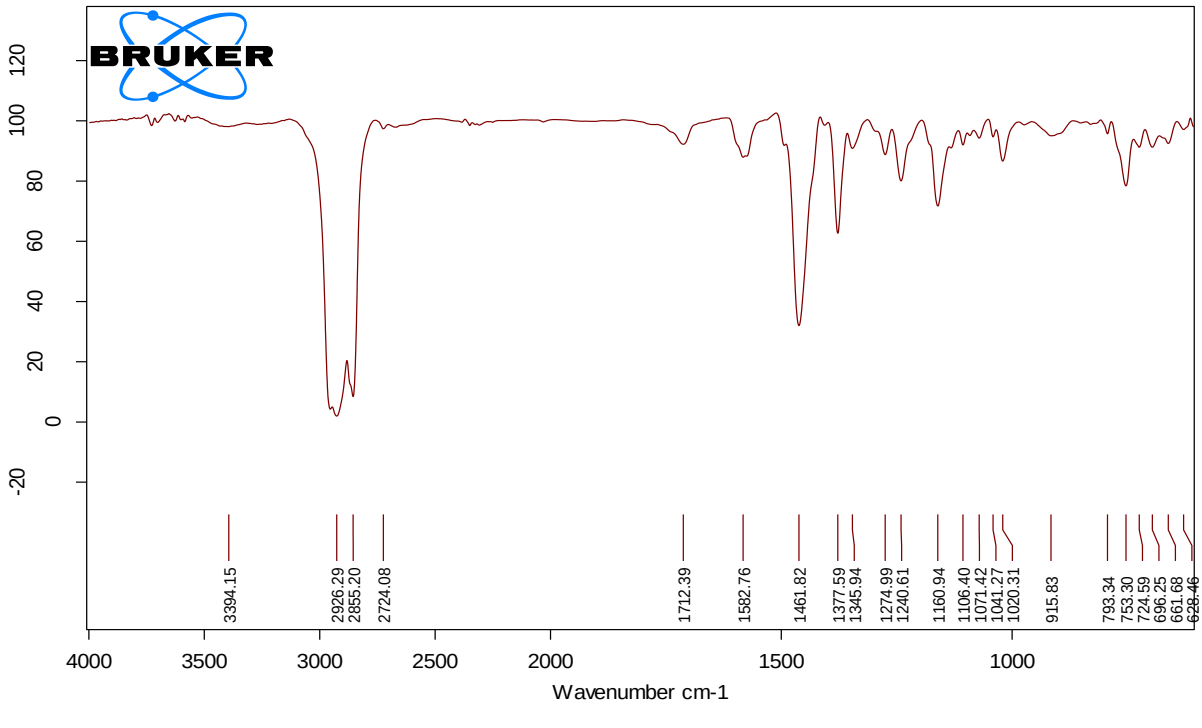
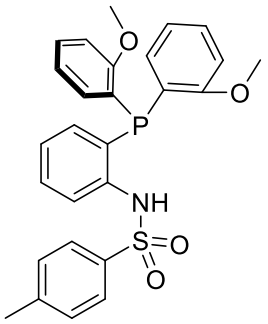


**Figure S9:** IR of ligand 2-(bis(2-methoxyphenyl)phosphaneyl)-4-methyl-*N*-phenylbenzenesulfonamide (**L2A**) in Nujol.

## 2.3. Synthesis of *N*-(2-(bis(2-methoxyphenyl)phosphanyl)phenyl)-4-methylbenzenesulfonamide (L1A):




*N*-(2-bromophenyl)-4-methylbenzenesulfonamide (2 gm, 6.13 mmol)was dissolved in THF (60 mL) and the reaction mixture was maintained at -84 ºC. *n*-BuLi (2 M) (6.23 mL, 12.26 mmol) was added drop wise with constant stirring. Reaction mixture was stirred for 30 minutes at -84 ºC. Next,chlorobis(2-methoxyphenyl)phosphane (1.71 gm, 6.13 mmol) in THF (60 mL) was added drop wise to the above lithiated reaction mixture at -84 ºC. Reaction mixture was further stirred overnight (16 hrs) at room temperature. THF was evaporated and the resultant residue was dissolved in DCM (160 mL). Subsequently, degassed water (80 mL) and HCl in diethyl ether (2 M) (3.06 mL, 6.13 mmol) were added and the mixture was stirred for 10 minutes. Organic layer was extracted under argon and dried on sodium sulfate. DCM was evaporated and crude residue was dried under vacuum for 2 hours. Compound **L1A**was purified by crystallization in DCM:hexaneat 0 ºC and was isolated in 85 % yield.

**$^{31}$P NMR** (500 MHz in $CDCl_3$): δ = - 47.46.**$^{1}$HNMR (**500 MHz in $CDCl_3$): δ = 8.16 (m, 1H, Ar-H), 7.73 (m, 1H, Ar-H), 7.52 (m, 2H, Ar-H), 7.31 (m, 3H, Ar-H), 6.98 (m, 1H, Ar-H), 6.86 (m, 5H, Ar-H/NH), 6.75 (m, 2H, Ar-H), 6.49 (m, 2H, Ar-H), 3.69 (s, 6H, *o*-OMe), 2.18 (s, 3H, *p*-Me). **$^{13}$C NMR** (125 MHz in $CDCl_3$): δ = 160.7. 160.6, 143.1, 141.4, 135.8, 135.7, 132.9, 130.3, 130.1, 129.2, 127.1, 126.4, 124.7, 122.8, 120.9, 110.1, 55.6, 21.4. **ESI-MS:** Calculated *m/z* for$[C_{27}H_{27}O_4NPS]^+$ = 492.1393 $[M+H]^+$; found *m/z* =492.1392 $[M+H]^+$.

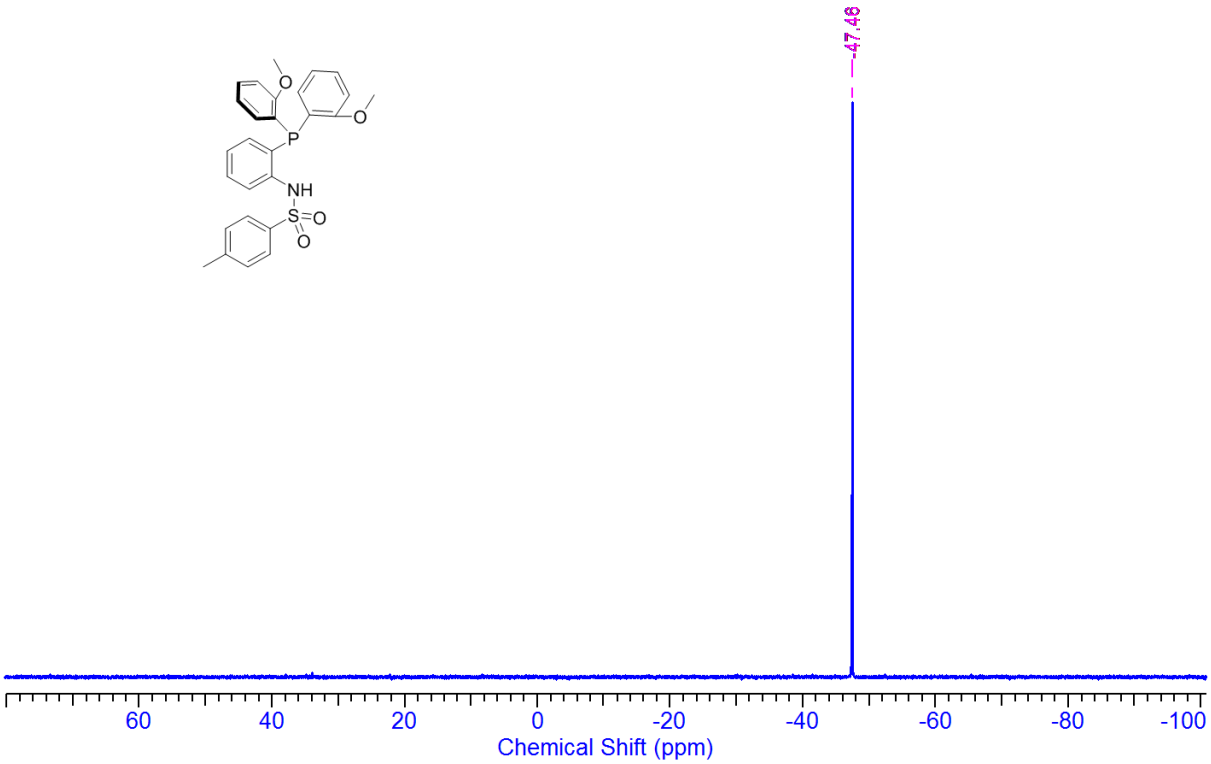



**Figure S10:** $^{31}$P NMR spectrum of ligand *N*-(2-(bis(2-methoxyphenyl)phosphaneyl)phenyl)-4-methylbenzenesulfonamide (**L1A**).

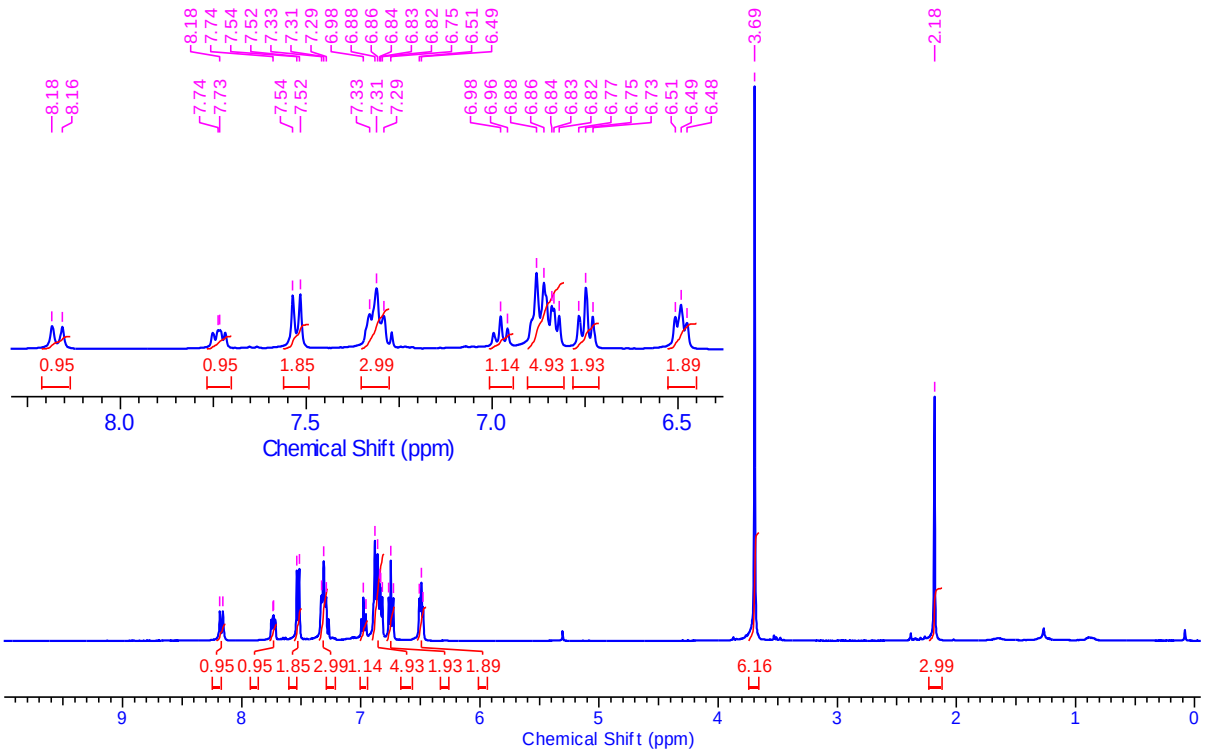



**Figure S11:** $^{1}$H NMR spectrum of ligand *N*-(2-(bis(2-methoxyphenyl)phosphaneyl)phenyl)-4-methylbenzenesulfonamide (**L1A**).

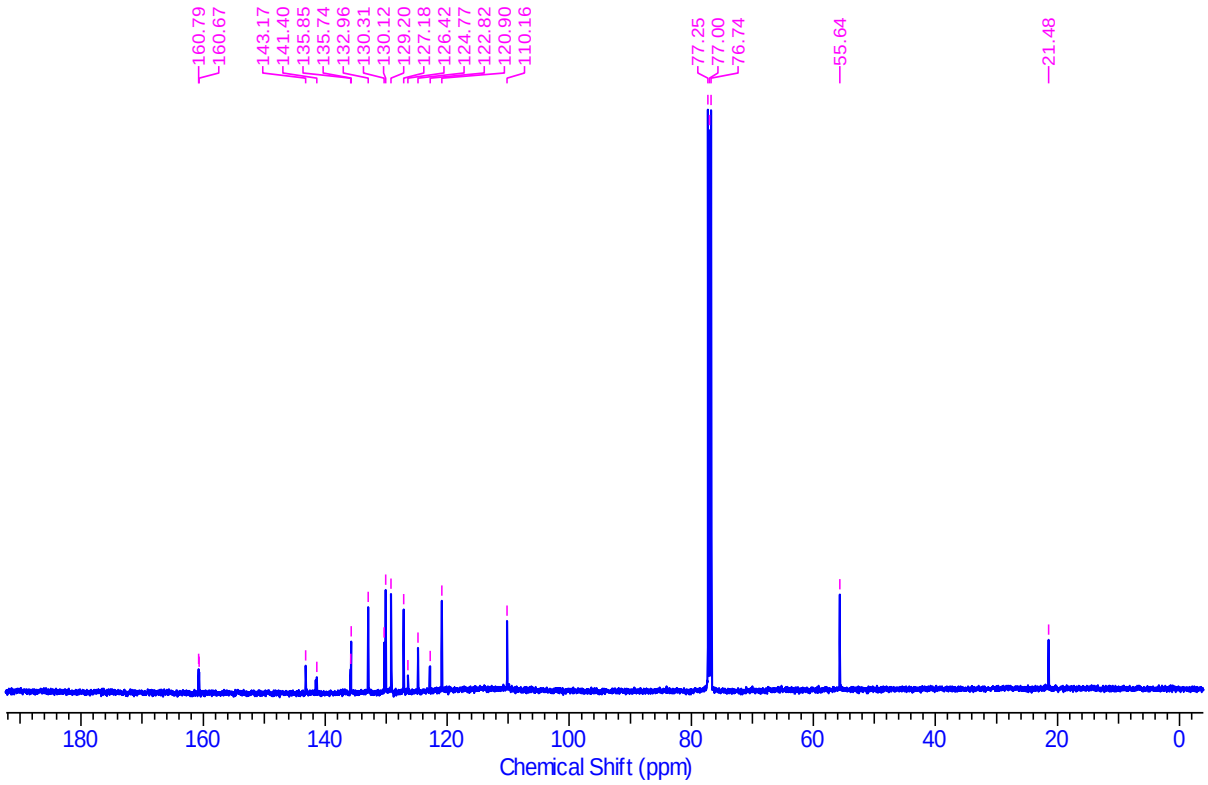



**Figure S12:** $^{13}$C NMR spectrum of ligand *N*-(2-(bis(2-methoxyphenyl)phosphaneyl)phenyl)-4-methylbenzenesulfonamide (**L1A**).

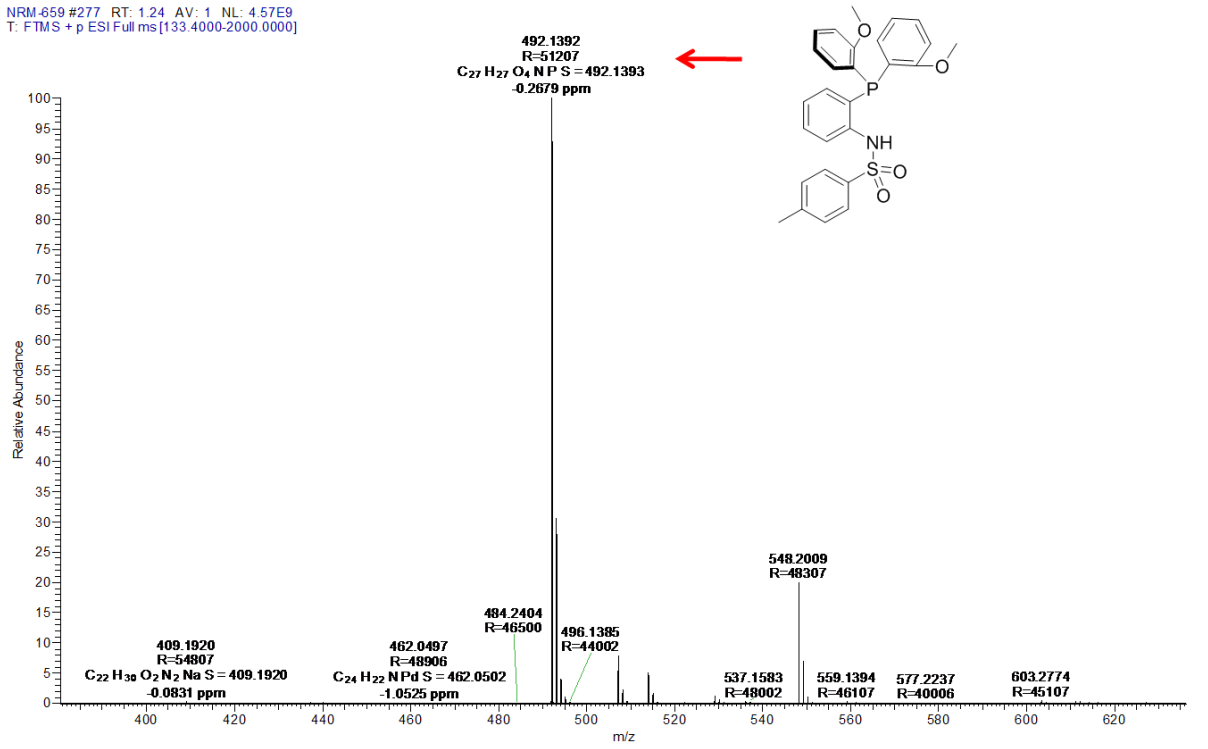



**Figure S13:** ESI-MS of ligand *N*-(2-(bis(2-methoxyphenyl)phosphaneyl)phenyl)-4-methylbenzenesulfonamide (**L1A**).

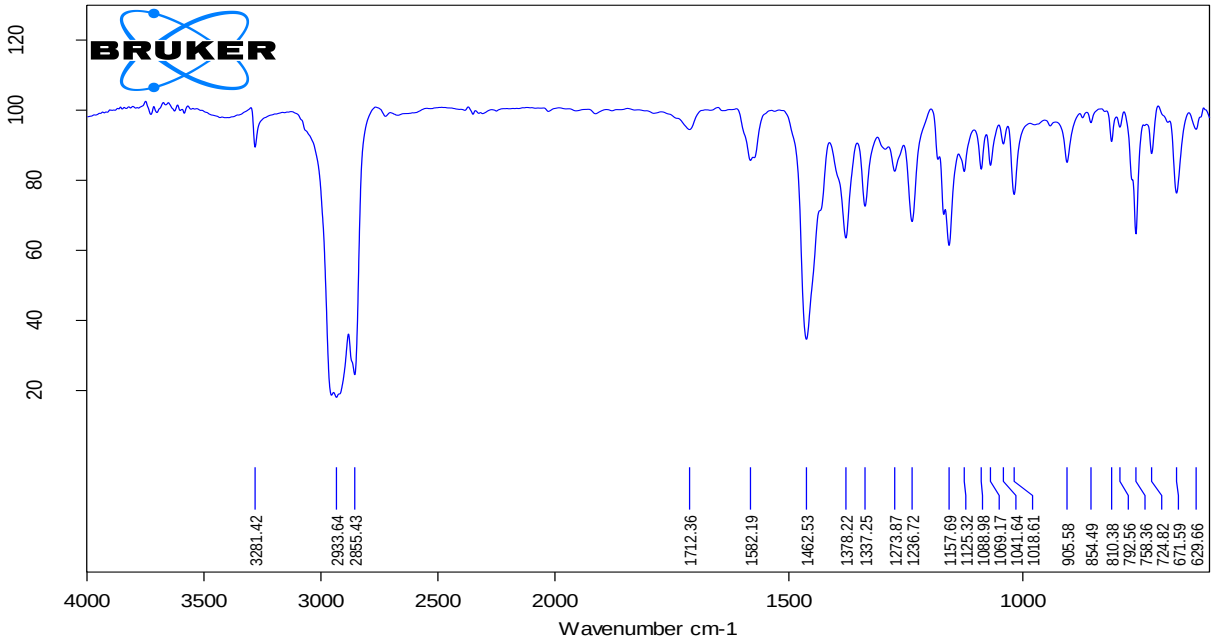



**Figure S14:** IR spectrum of ligand N-(2-(bis(2-methoxyphenyl)phosphaneyl)phenyl)-4-methylbenzenesulfonamide (**L1A**) in Nujol.

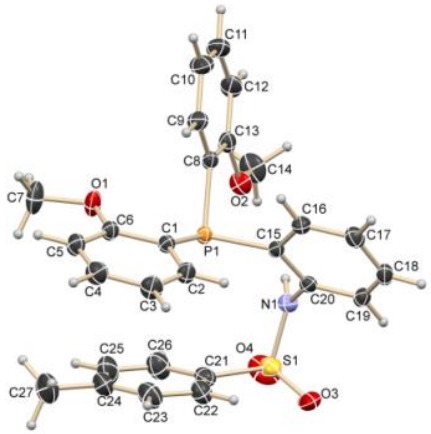


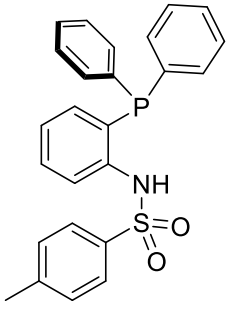

**Figure S15:** Single crystal of ligand *N*-(2-(bis(2-methoxyphenyl)phosphaneyl)phenyl)-4-methylbenzenesulfonamide (**L1A**).[Thermal ellipsoids are drawn at 50% probability]

**Table S1.** Crystal data and structure refinement for (**L1A**).

| | |
|---|---|
| Identification code | **L1A** |
| Empirical formula | C27 H26 N O4 P S |
| Formula weight | 491.52 |
| Temperature | 100(2) K |
| Wavelength | 0.71073 Å |

| | | |
|---|---|---|
| Crystal system | Triclinic | |
| Space group | P-1 | |
| Unit cell dimensions | a = 9.5013(4) Å | α= 73.562(2)°. |
| | b = 10.9649(4) Å | β= 70.075(2)°. |
| | c = 13.6934(5) Å | γ = 71.803(2)°. |
| Volume | 1248.98(9) $Å^3$ | |
| Z | 2 | |
| Density (calculated) | 1.307 $Mg/m^3$ | |
| Absorption coefficient | 0.227 $mm^{-1}$ | |
| F(000) | 516 | |
| Crystal size | 0.200 x 0.170 x 0.030 $mm^3$ | |
| Theta range for data collection | 1.994 to 30.800°. | |
| Index ranges | -12<=h<=13, -14<=k<=15, -19<=l<=19 | |
| Reflections collected | 19104 | |
| Independent reflections | 7686 [R(int) = 0.0211] | |
| Completeness to theta = 25.242° | 99.8 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.993 and 0.956 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 7686 / 0 / 283 | |
| Goodness-of-fit on $F^2$ | 1.030 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0473, wR2 = 0.1235 | |
| R indices (all data) | R1 = 0.0625, wR2 = 0.1342 | |
| Extinction coefficient | n/a | |
| Largest diff. peak and hole | 0.558 and -0.557 $e.Å^{-3}$ | |

## 2.4. Synthesis of *N*-(2-(diphenylphosphanyl)phenyl)-4-methylbenzenesulfonamide (L1B):



*N*-(2-bromophenyl)-4-methylbenzenesulfonamide (1 gm, 3.06 mmol)was dissolved in THF (30 mL) and the content was cooled to -84 ºC. *n*-BuLi (2 M) (3.06 mL, 6.13 mmol) was added drop wise with constant stirring. The reaction mixture was stirred for 30 minutes at -84 ºC. Next,chlorodiphenylphosphane (0.56 mL, 3.06 mmol) was added drop wise to the above lithiated reaction mixture at -84 ºC. This mixture was further stirred overnight (16 hours) at room temperature. THF was evaporated and the resultant residue was dissolved in DCM (60 mL). Subsequently, degassed water (30 mL) and HCl in diethyl ether (2 M) (1.53 mL, 3.06 mmol) was added and the mixture was stirred for 10 minutes. Organic layer was extracted under argon and dried on pre-dried sodium sulfate. Volatiles were stripped off and crude residue was dried under vacuum for 2 hours. Compound was purified by crystallization in DCM:hexaneat 0 ºC and was isolated in 74 % yield.

**$^{31}$P NMR** (500 MHz in $CDCl_3$): δ = -26.44.**$^{1}$H NMR** (500 MHz in $CDCl_3$): δ = 7.82 (s, 1H, Ar-H), 7.74 (m, 1H, Ar-H), 7.49 (s, 2H, Ar-H), 7.33 (m, 3H, Ar-H/NH), 7.26 (m, 4H, Ar-H), 7.03(m, 5H, Ar-H), 6.97 (s, 2H, Ar-H), 6.88 (m, 1H, Ar-H), 2.29 (s, 3H, *p*-Me). **$^{13}$C NMR** (125 MHz in $CDCl_3$): δ = 143.5, 135, 133.4, 133.1, 130.5, 129.3, 128.9, 128.7, 128.5, 125.1, 121, 21.5, **ESI-MS:** Calculated *m/z* for$[C_{25}H_{23}NO_2PS]^+$432.1187; found *m/z* = 432.1175 $[M+H]^+$. Calculated *m/z* for$[C_{25}H_{22}NO_2PSNa]^+$= 454.1007; found m/z = 454.0990 $[M+Na]^+$.

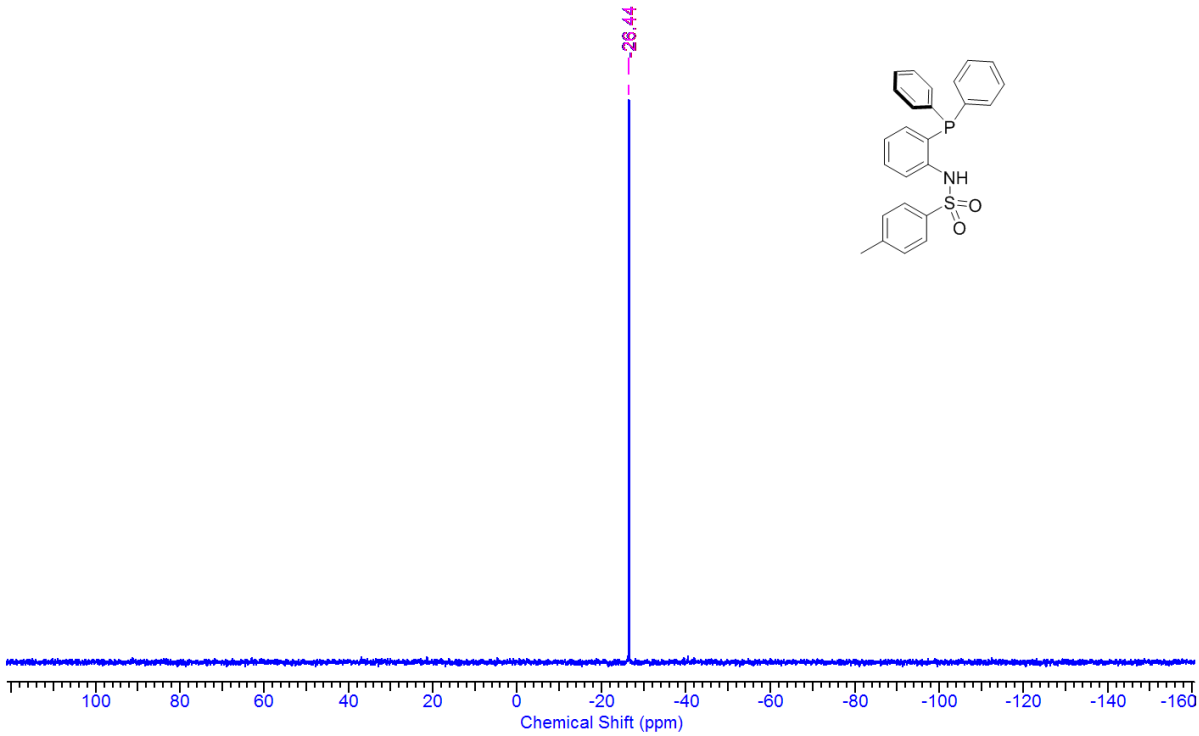



**Figure S16:** $^{31}$P NMR spectrum of ligand *N*-(2-(diphenylphosphanyl)phenyl)-4-methylbenzenesulfonamide (**L1B**).

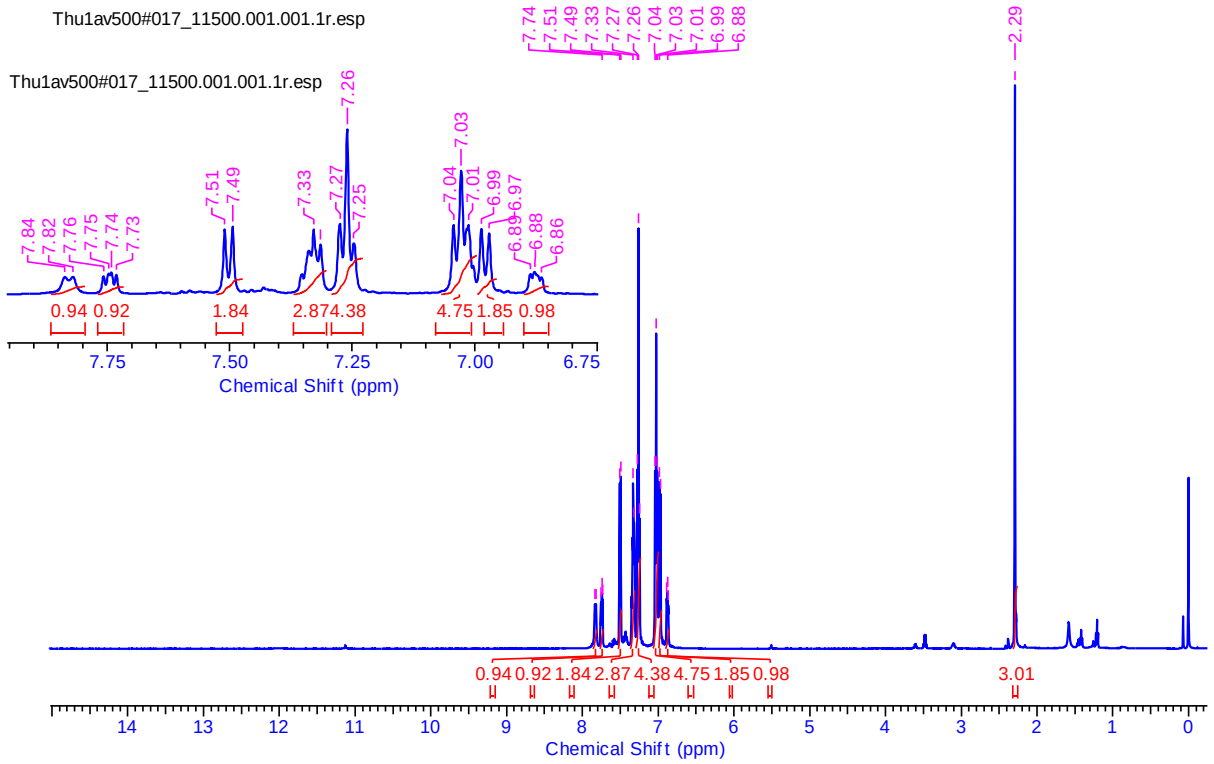



**Figure S17:** $^{1}$H NMR spectrum of ligand *N*-(2-(diphenylphosphanyl)phenyl)-4-methylbenzenesulfonamide (**L1B**).

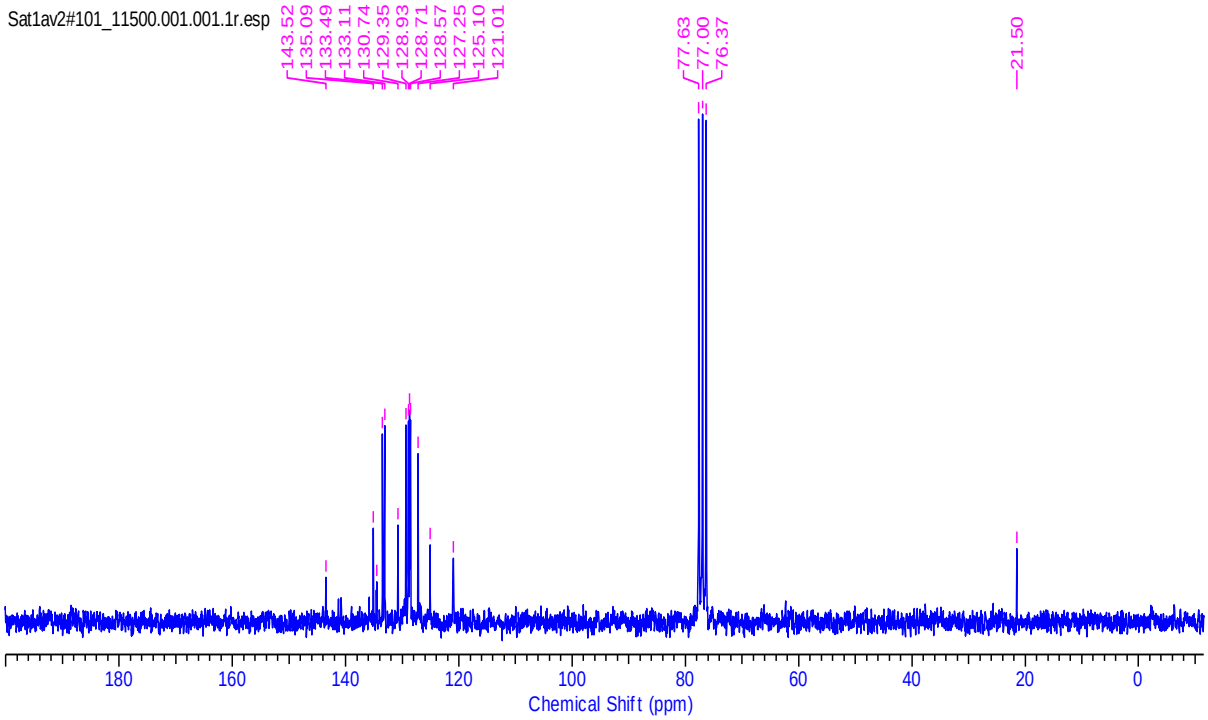



**Figure S18:** $^{13}$C NMR of ligand *N*-(2-(diphenylphosphanyl)phenyl)-4-methylbenzenesulfonamide (**L1B**).

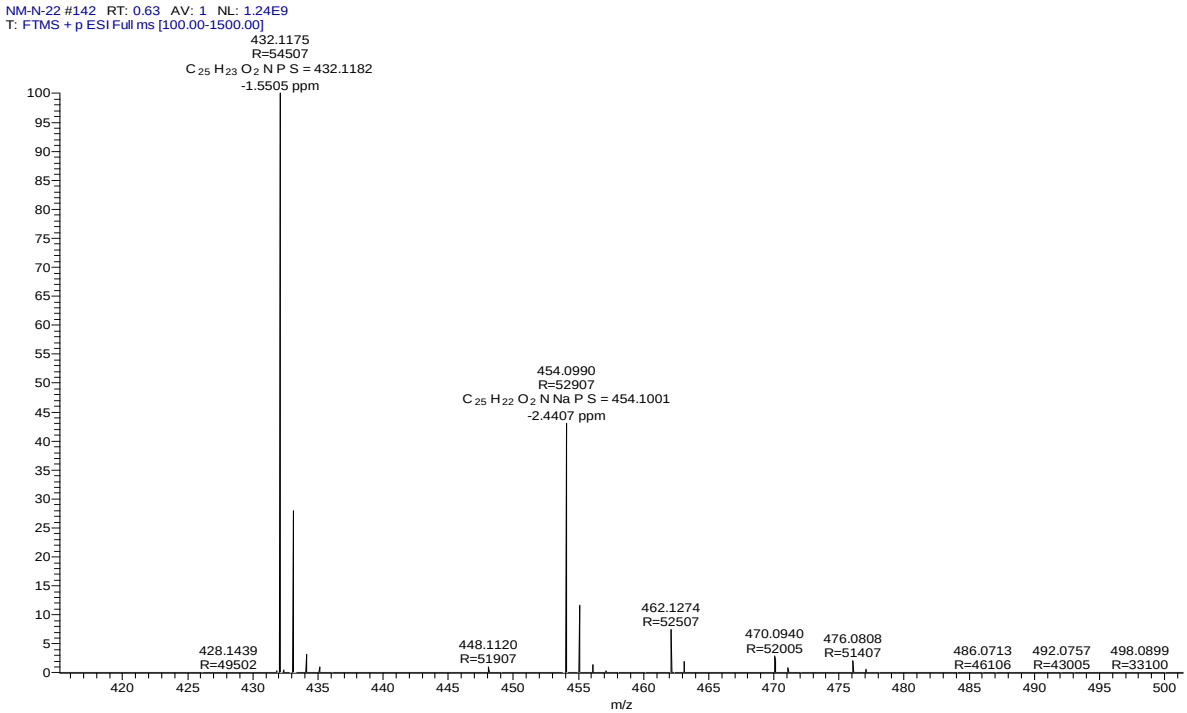



**Figure S19:** ESI-MS of ligand *N*-(2-(diphenylphosphanyl)phenyl)-4-methylbenzenesulfonamide (**L1B**).

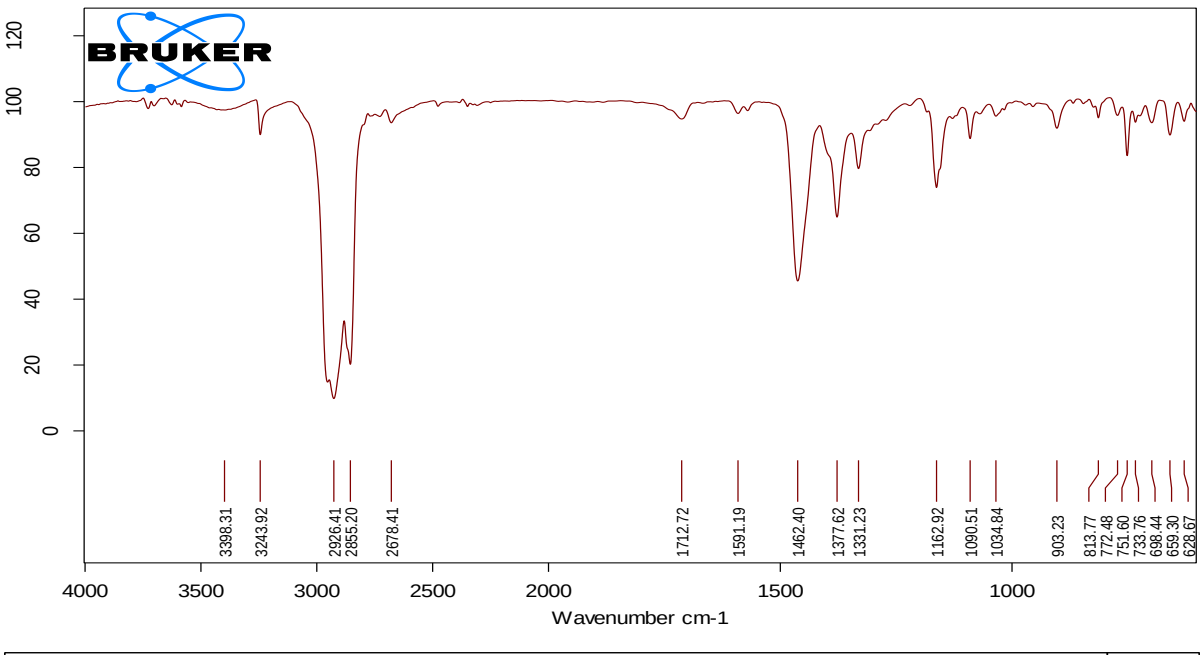



**Figure S20:** IR spectrum of ligand *N*-(2-(diphenylphosphanyl)phenyl)-4-methylbenzenesulfonamide (**L1B**) in Nujol.

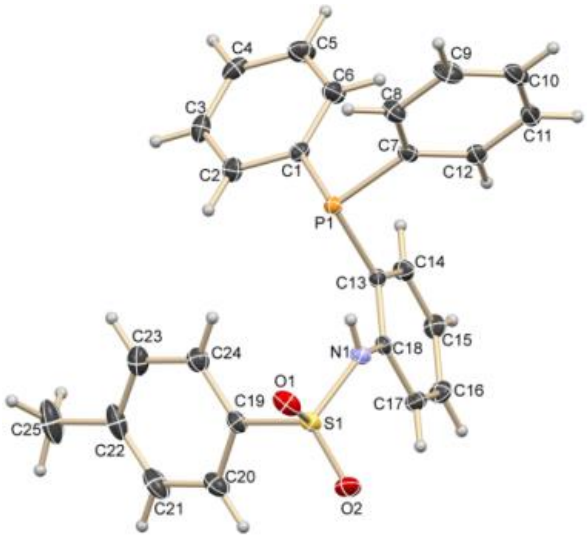


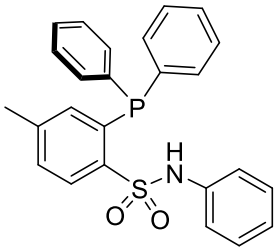

**Figure S21:** Molecular structure of ligand *N*-(2-(diphenylphosphanyl)phenyl)-4-methylbenzenesulfonamide (**L-1a**).Thermal ellipsoids are drawn at 50% probability level.

**Table S2**. Crystal data and structure refinement for (**L1B**).

| | |
|---|---|
| Identification code | **L1B** |
| Empirical formula | C25 H22 N O2 P S |
| Formula weight | 431.46 |
| Temperature | 100(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Triclinic |

| | | |
|---|---|---|
| Space group | P-1 | |
| Unit cell dimensions | a = 10.0641(6) Å | α= 76.414(2)°. |
| | b = 10.8548(6) Å | β= 81.176(2)°. |
| | c = 11.1095(6) Å | γ = 65.105(2)°. |
| Volume | 1068.02(11) $Å^3$ | |
| Z | 2 | |
| Density (calculated) | 1.342 $Mg/m^3$ | |
| Absorption coefficient | 0.249 $mm^{-1}$ | |
| F(000) | 452 | |
| Crystal size | 0.190 x 0.110 x 0.070 $mm^3$ | |
| Theta range for data collection | 2.683 to 28.000°. | |
| Index ranges | -13<=h<=13, -14<=k<=14, -14<=l<=14 | |
| Reflections collected | 71397 | |
| Independent reflections | 5123 [R(int) = 0.0305] | |
| Completeness to theta = 25.242° | 99.4 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.983 and 0.954 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 5123 / 0 / 276 | |
| Goodness-of-fit on $F^2$ | 1.052 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0348, wR2 = 0.0852 | |
| R indices (all data) | R1 = 0.0367, wR2 = 0.0865 | |
| Extinction coefficient | n/a | |
| Largest diff. peak and hole | 1.176 and -0.330 $e.Å^{-3}$ | |

## 2.5. Synthesis of 2-(diphenylphosphanyl)-4-methyl-*N*-phenylbenzenesulfonamide (L2B):



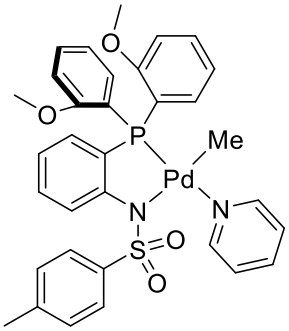

*N*-(2-bromophenyl)-4-methylbenzenesulfonamide (0.5 gm, 1.53 mmol)was dissolved in THF (15 mL) and the content was cooled to -41 ºC. *n*-BuLi (2 M) (1.53 mL, 3.06 mmol) was added drop wise with constant stirring. This mixture was stirred for 3 hours. Next,chlorodiphenylphosphane (0.28 mL, 1.53 mmol) was added drop wise to the above lithiated reaction mixture at -41 ºC. The reaction mixture was further stirred overnight (16

hours) at room temperature. Volatiles were evaporated and the resultant residue was dissolved in DCM (40 mL). Subsequently, degassed water (20 mL) andHCl in diethyl ether (2 M) (0.76 mL, 1.53 mmol) was added and the mixture was stirred for 10 minutes. Organic layer was extracted under argon and dried on pre-dried sodium sulfate. DCM was evaporated and crude residue was dried under vacuum for 2 hours. The resultant solid was purified by crystallization in DCM:hexaneat 0 ºC. The analytical data matches with reported similar ligands.[6]

**$^{31}$P NMR** (500 MHz in $CDCl_3$): δ = -9.

**3.Synthesis of palladium complexes**

## 3.1. Palladium complex C1:




Equimolar mixture of ligand **L1A** (0.100 gm, 0.20 mmol) and [(TMEDA)$PdMe_2$] (0.051gm, 0.20 mmol) was taken in a Schlenk tube and 5 mL pyridine was added. The reaction mixture was stirred at room temperature for 2 hours and volatiles were evaporated. Again, pyridine was added (5 mL), mixture was stirred and volatiles were evaporated. This procedure was repeated for three times and solid was dried under vacuum for 1 hour. The resultant solid was washed with diethyl ether (5 mL * 2) to obtain 91 % of anticipated complex **C1**.

**$^{31}$P NMR** (400 MHz in $CDCl_3$): δ = 26.34. **$^{1}$H NMR** (400 MHz in $CDCl_3$): δ = 8.89 (d, 2H, *J* = 4.88 Hz), 7.74 (t, 1H, *J* = 7.63 Hz), 7.63 (s, 1H), 7.46 (t, 2H, *J* = 7.63 Hz), 7.37 (m, 4H), 7.13 (t, 1H, *J* = 7.63 Hz), 6.99 (br. s, 2H), 6.92 (q, 2H, *J* = 7.93, 4.88 Hz), 6.85 (s, 2H), 6.79 (s, 1H), 6.72 (d, 2H, *J* = 7.32 Hz), 6.60 (m, 1H), 3.71 (s, 6H, *o*-OMe), 2.18 (s, 3H, *p*-OMe), 0.32 (s, 3H, Pd-Me). **$^{13}$C NMR** (100 MHz in $CDCl_3$): δ = 160.8, 160.7, 151.2, 140.9, 139.7, 137.1, 135.2, 132.2, 131.5, 128.2, 127.1, 124.9, 124.3, 121.2, 121.1, 120.6, 120.5, 119.2, 117.8, 117.2, 111.2, 55.5, 21.2, -2.7. **ESI-MS:** Calculated *m/z* for$[C_{33}H_{34}N_2O_4PPdS]^+$= 691.1012 $[M+H]^+$; found *m/z* = 691.0795 $[M+H]^+$. Calculated *m/z* for $[C_{28}H_{29}NO_4PPdS]^+$ = 612.0584 $[(M-Py)+H]^+$; found *m/z* = 612.0593 $[(M-Py)+H]^+$. **Elemental analysis (%):** Calculated for $C_{33}H_{33}N_2O_4PPdS$: C, 57.35; H, 4.81; N, 4.05; found: C, 57.94; H, 5.11; N, 3.90.

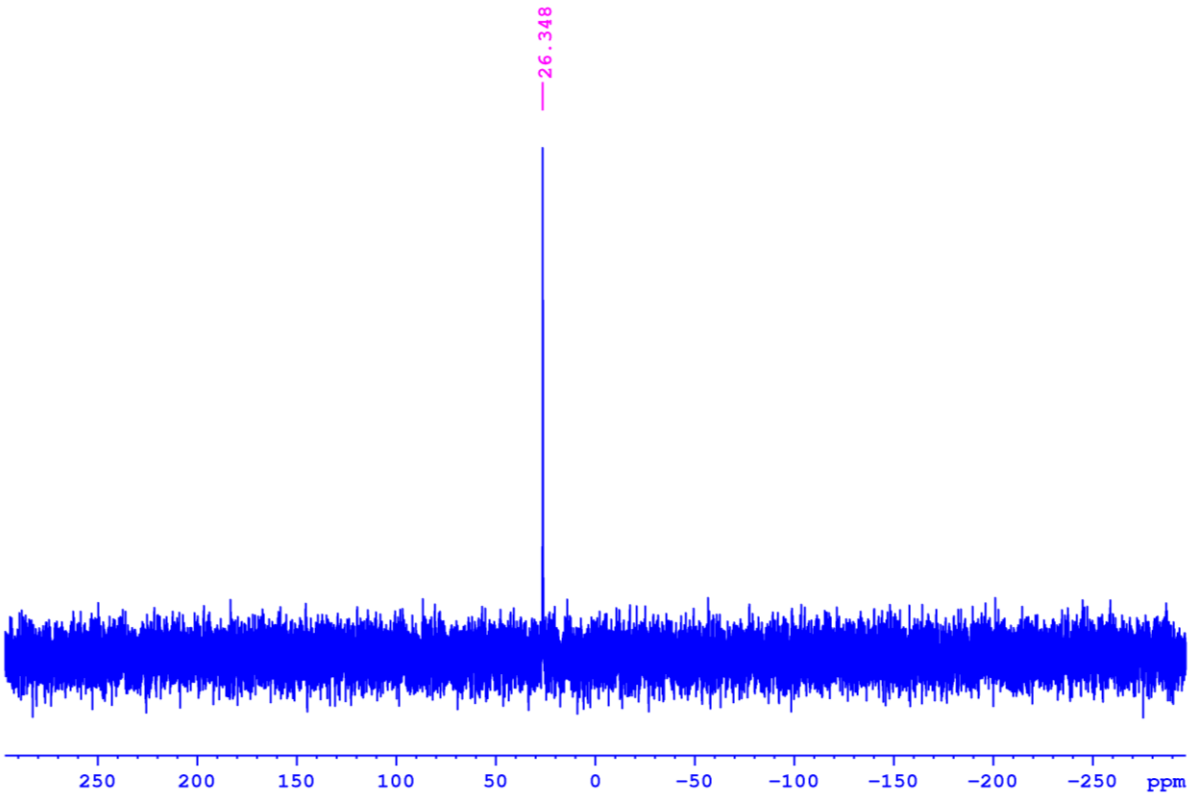



**Figure S22:** $^{31}$P NMR spectrum of complex **C1** in $CDCl_3$.

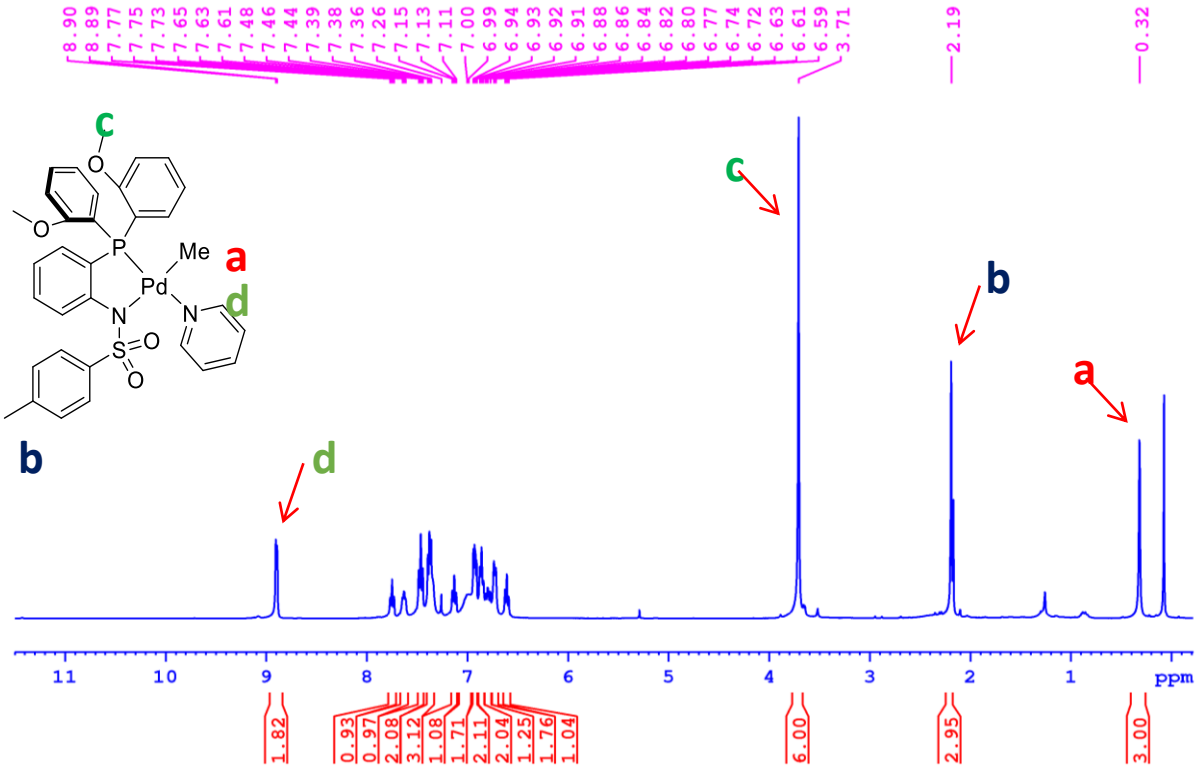



**Figure S23:** $^{1}$H NMR spectrum of complex**C1** in $CDCl_3$.

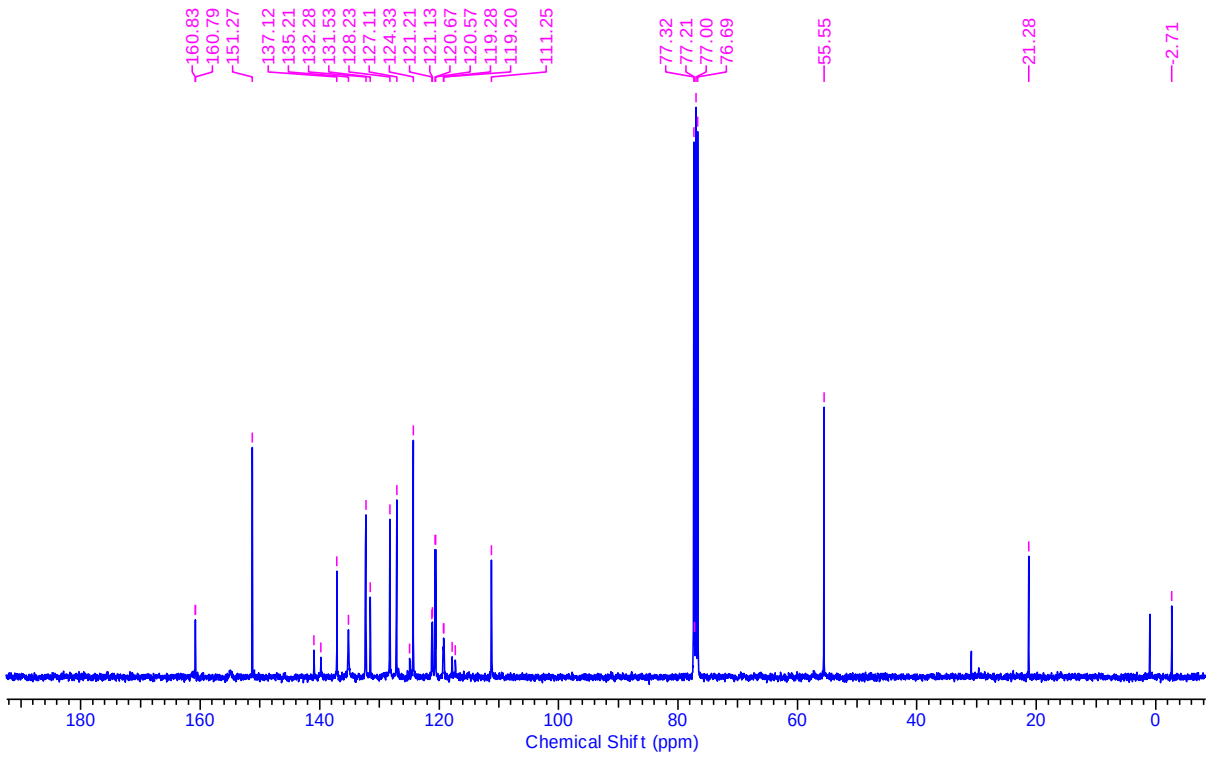



**Figure S24:** $^{13}$CNMR spectrum of complex **C1** in $CDCl_3$.

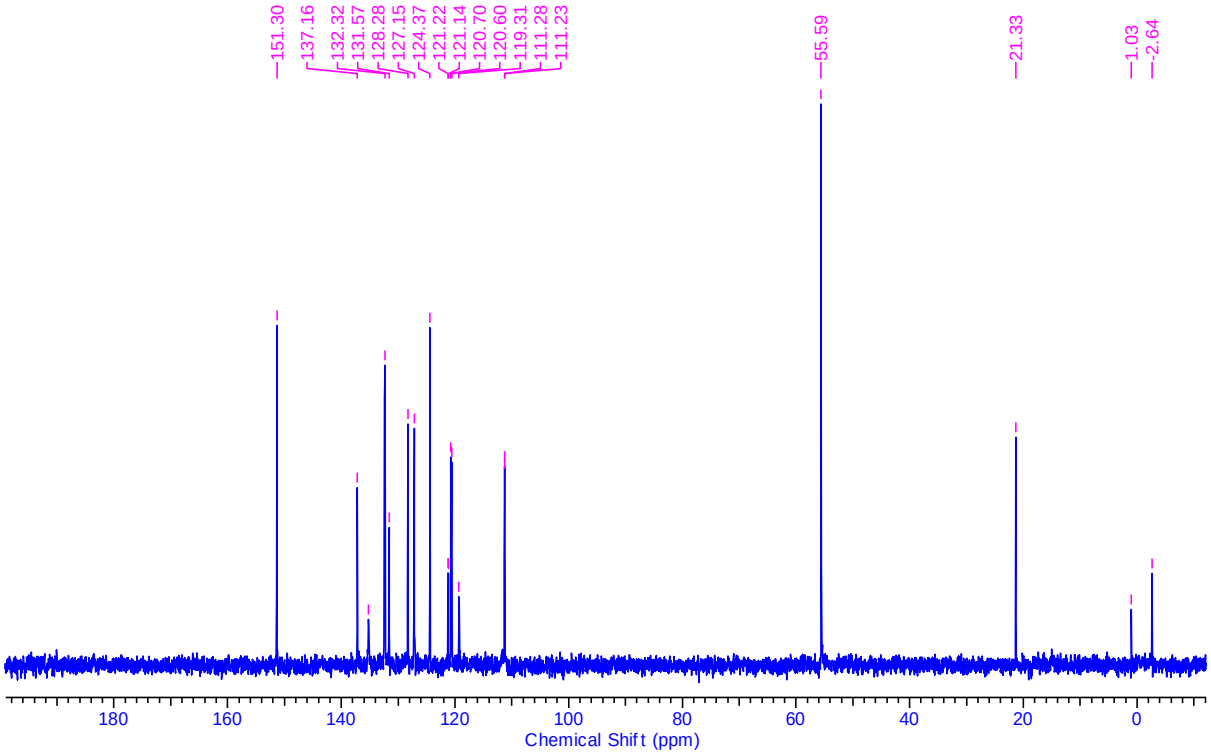



**Figure S25:** DEPT NMR spectrum of complex **C1** in $CDCl_3$.

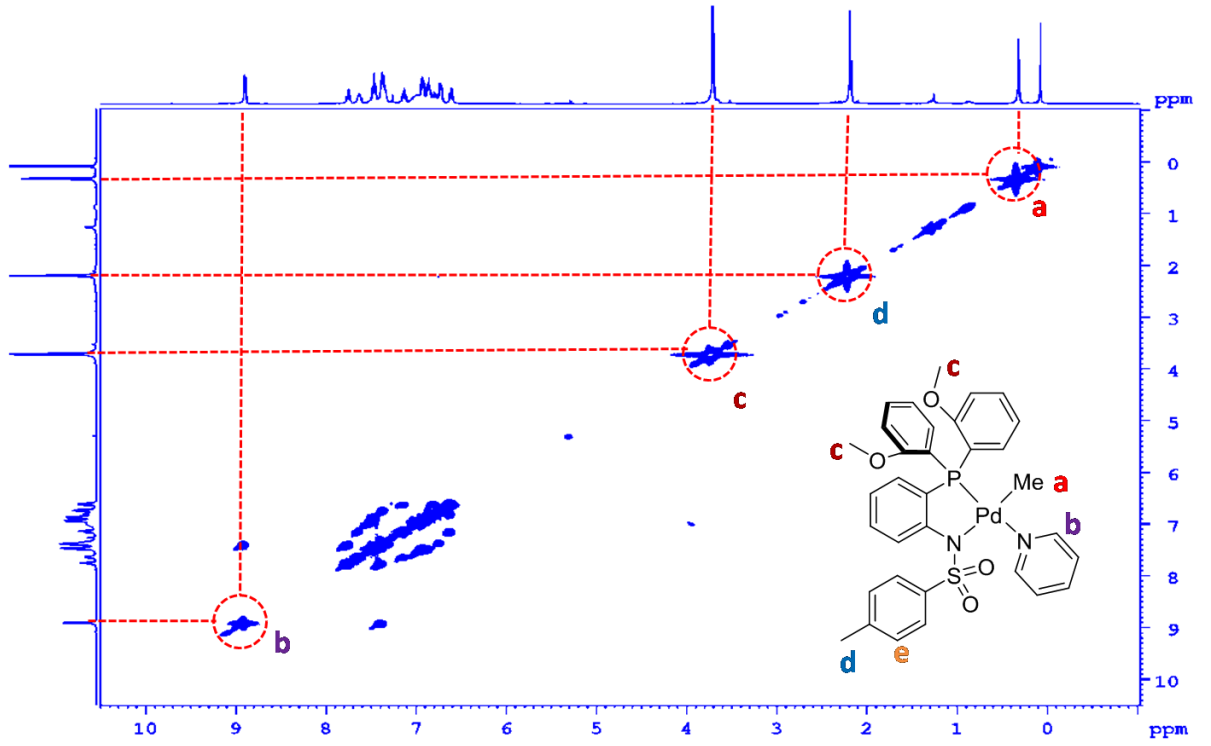



**Figure S26:** COSY-NMR spectrum of complex **C1** in $CDCl_3$.

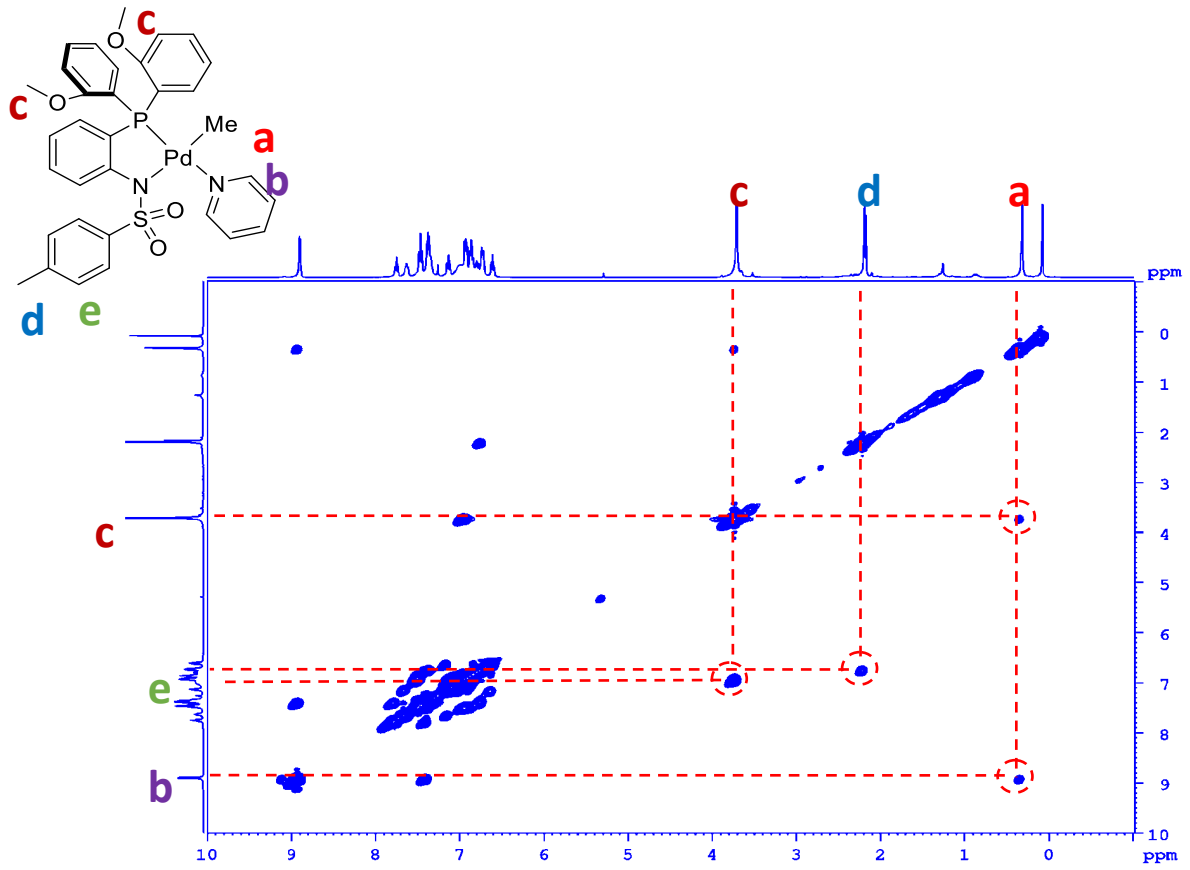



**Figure S27:** NOESY-NMR spectrum of complex **C1** in $CDCl_3$.

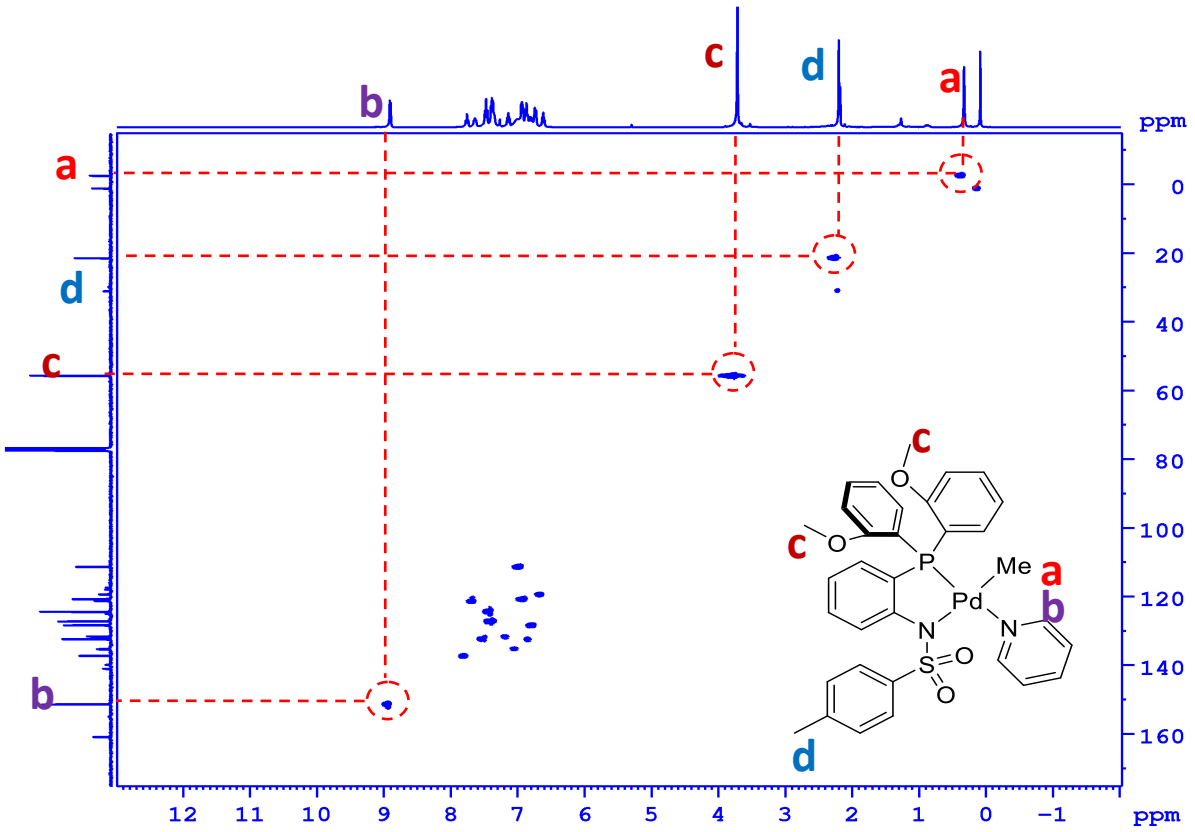



**Figure S28:** Direct C-H correlation (HSQC) NMR spectrum of complex**C1** in $CDCl_3$.

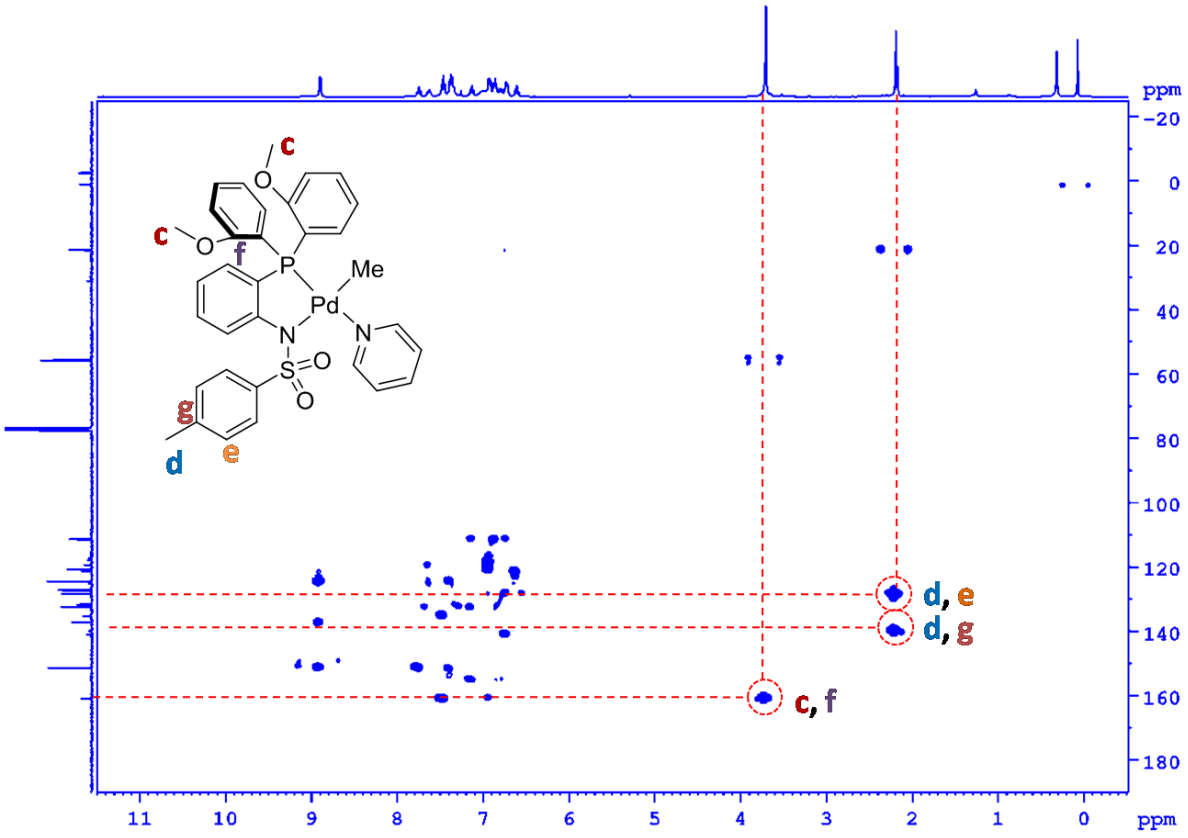



**Figure S29:** Long range C-H (HMBC) correlation NMR spectrum of complex **C1** in $CDCl_3$.

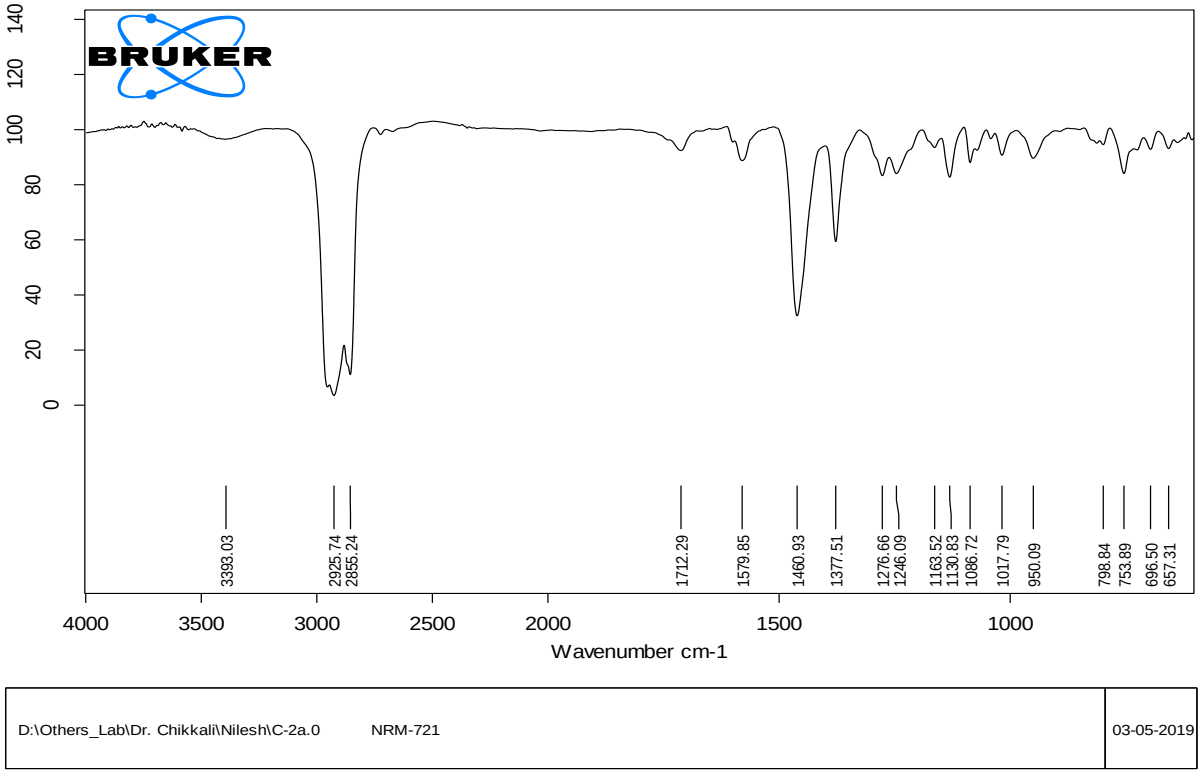



**Figure S30:** IR spectrum of complex **C1** in Nujol.

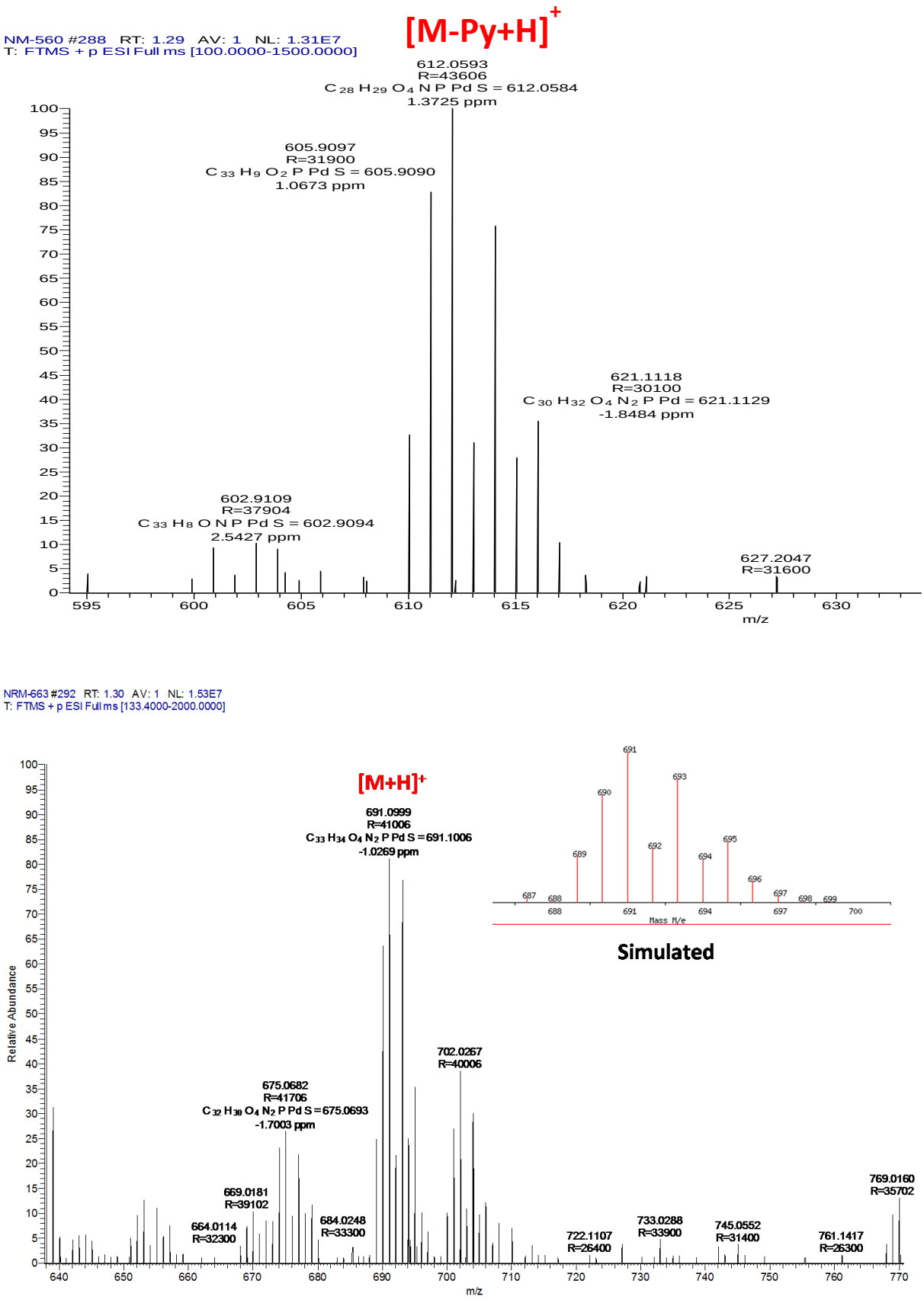



**Figure S31:** ESI-MS spectrum of complex **C1** ($[M\text{-}Py+H]^+$ (top) and $[M+H]^+$ (bottom).

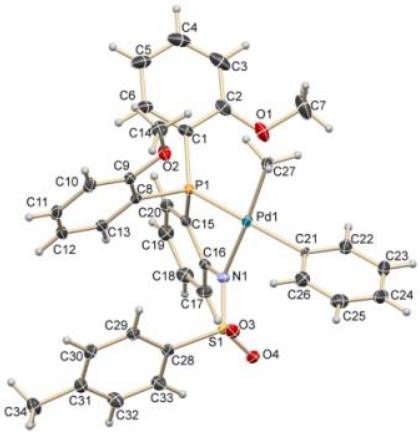


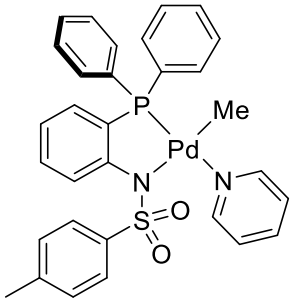

**Figure S32:** Molecular structure of complex**C1**. Thermal ellipsoids are drawn at 50% probability level.

**Table S3.** Crystal data and structure refinement for **C1**.

| | | |
|---|---|---|
| Identification code | **C1** | |
| Empirical formula | C33 H33 N2 O4 P Pd S | |
| Formula weight | 691.04 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | $P2_1/c$ | |
| Unit cell dimensions | a = 12.3236(13) Å | α= 90°. |
| | b = 18.867(2) Å | β= 105.039(4)°. |
| | c = 13.3975(15) Å | γ = 90°. |
| Volume | 3008.4(6) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.526 $Mg/m^3$ | |
| Absorption coefficient | 0.781 $mm^{-1}$ | |
| F(000) | 1416 | |
| Crystal size | 0.190 x 0.030 x 0.020 $mm^3$ | |
| Theta range for data collection | 2.672 to 27.998°. | |
| Index ranges | -16<=h<=16, -24<=k<=24, -17<=l<=17 | |
| Reflections collected | 160280 | |
| Independent reflections | 7256 [R(int) = 0.0441] | |
| Completeness to theta = 25.242° | 99.7 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.985 and 0.866 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 7256 / 0 / 383 | |

| | |
|---|---|
| Goodness-of-fit on $F^2$ | 1.075 |
| Final R indices [I>2sigma(I)] | R1 = 0.0237, wR2 = 0.0568 |
| R indices (all data) | R1 = 0.0274, wR2 = 0.0605 |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 1.189 and -1.012 e.$Å^{-3}$ |

## 3.2. Palladium complex C2:




Equimolar mixture of ligand **L1B** (0.855 gm, 1.98 mmol)and [(TMEDA)$PdMe_2$] (0.500 gm, 1.98 mmol) was taken in a Schlenk tube and 8 mL pyridine was added. The content was stirred at room temperature for 3 hours and volatiles were evaporated. Next, pyridine (8 mL) was added, mixture was stirred and volatiles were evaporated. This procedure was repeated for 2 more times and the resultant solid was dried under vacuum for 4 hours. Finally, the anticipated compound was obtained in 92 % yield after washing with diethyl ether (3 * 5 mL) and drying.

**$^{31}$P NMR** (400 MHz in $CDCl_3$): δ = 40.84. **$^{1}$H NMR** (400 MHz in $CDCl_3$): δ = 8.89 (s, 2H, Ar-H). 7.78 (s, 2H, Ar-H), 7.37-7.44 (m, 12H, Ar-H), 7.31 (d, 2H, Ar-H), 7.22 (s, 1H, Ar-H), 6.83 (s, 1H, Ar-H), 6.72 (s, 1H, Ar-H), 6.65 (s, 2H, Ar-H), 2.15 (s, 3H, *p*-Me), 0.42 (s, 3H, Pd-Me). **$^{13}$C NMR** (100 MHz in $CDCl_3$): δ = 156.0,151, 137.4, 133.4, 133.3, 132.6, 130.4, 128.6, 128.4, 128.2, 126.7, 124.4, 122.7, 120.3, 21.2, -2.4. **ESI-MS:** Calculated *m/z* for$[C_{31}H_{30}N_2O_2PPdS]^+$= 631.0795 $[M+H]^+$; found *m/z* = 631.0795 $[M+H]^+$.

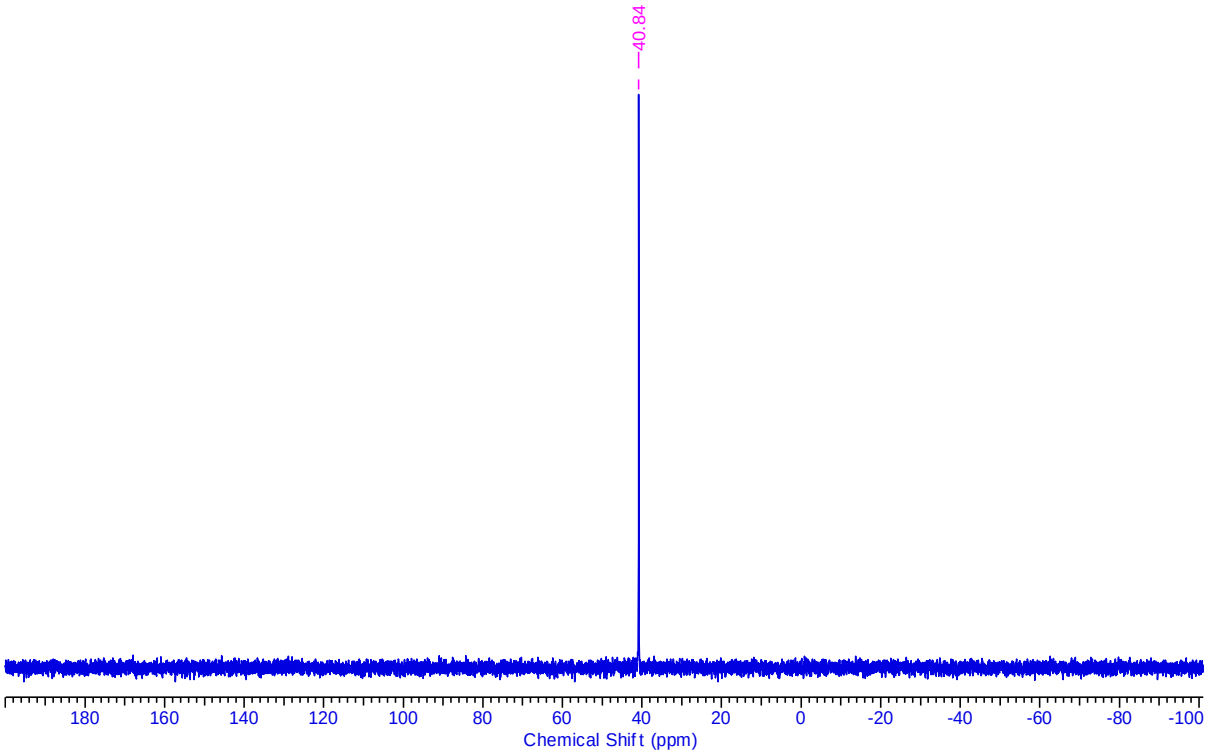



**Figure S33:** $^{31}$P NMR spectrum of complex **C2** in $CDCl_3$.

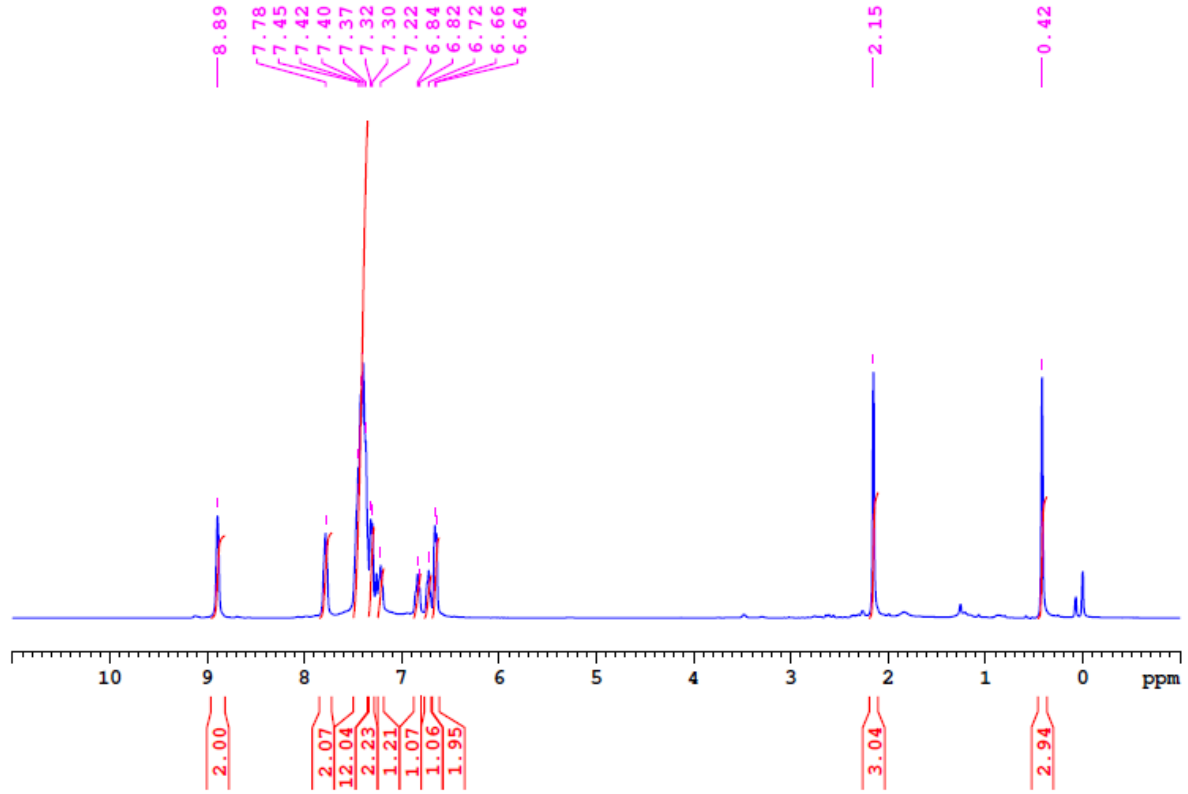



**Figure S34:** $^{1}$HNMR spectrum of complex **C2** in $CDCl_3$.

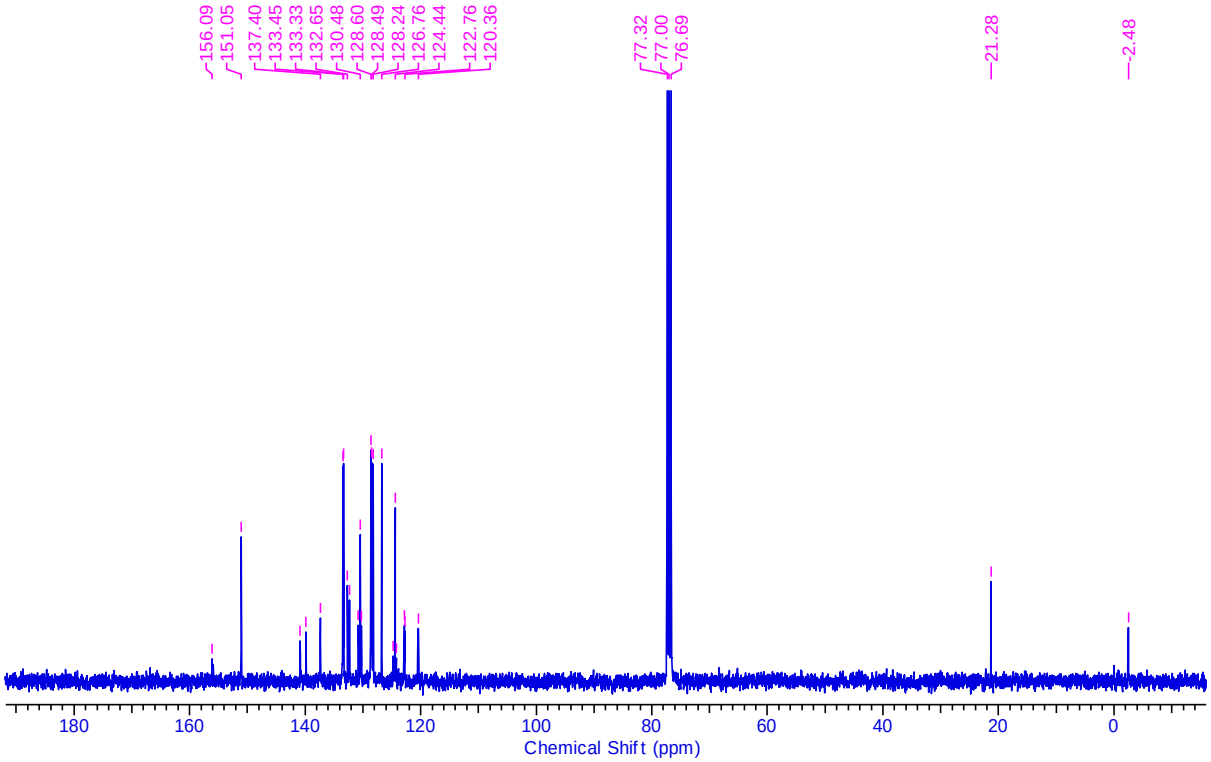



**Figure S35:** $^{13}C$ NMR spectrum of complex **C2** in $CDCl_3$.

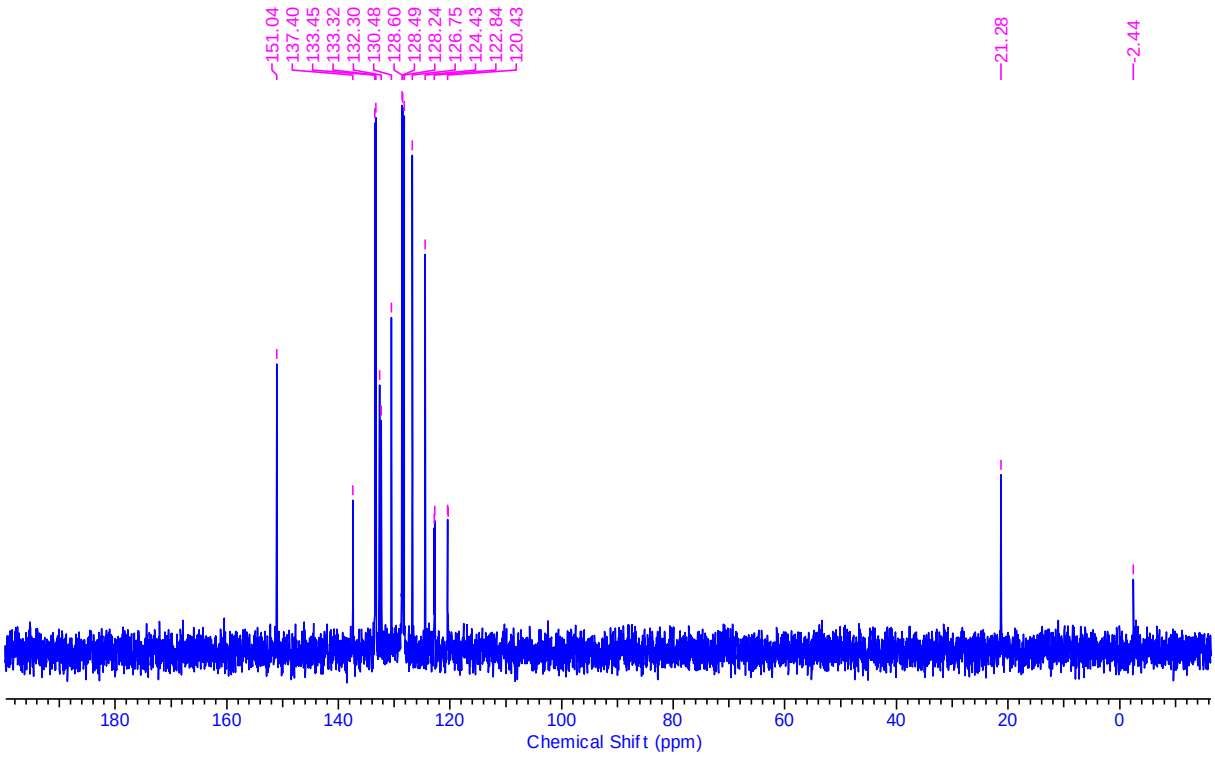



**Figure S36:** DEPT-NMR spectrum of complex **C2** in $CDCl_3$.

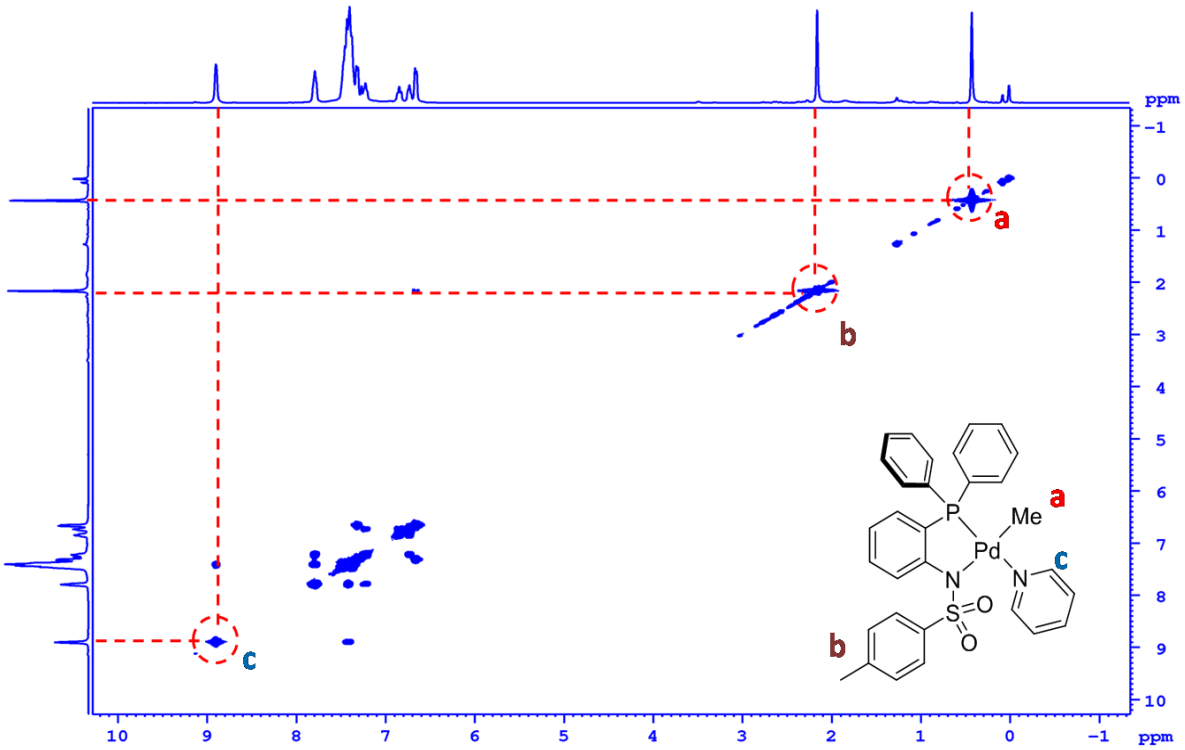



**Figure S37:** COSY-NMR spectrum of complex **C2** in $CDCl_3$.

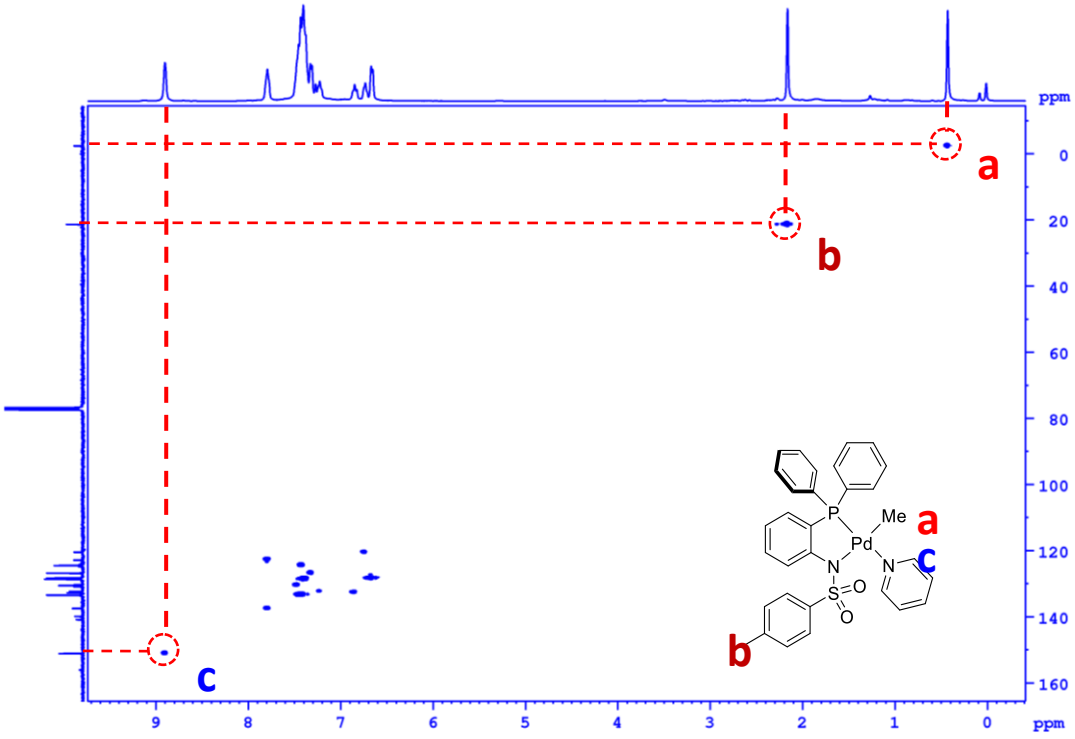



**Figure S38:** HSQC-NMR spectrum of complex **C2** in $CDCl_3$.

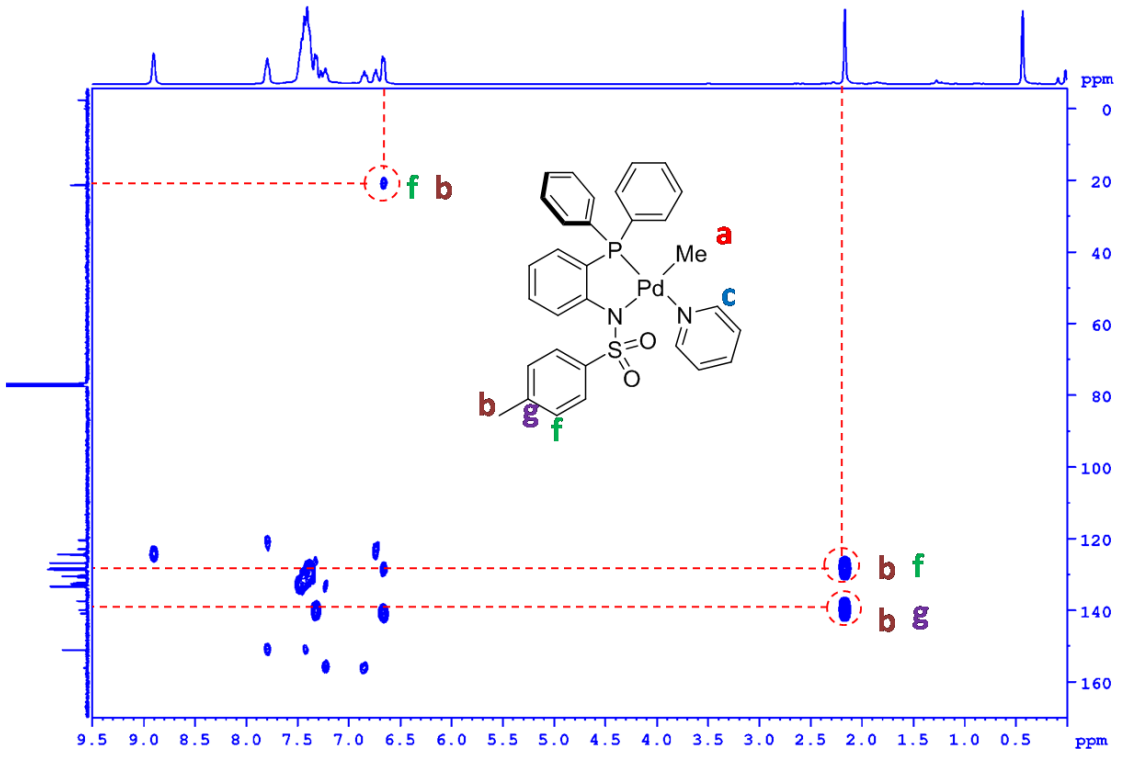



**Figure S39:** HMBC-NMR spectrum of complex **C2** in $CDCl_3$.

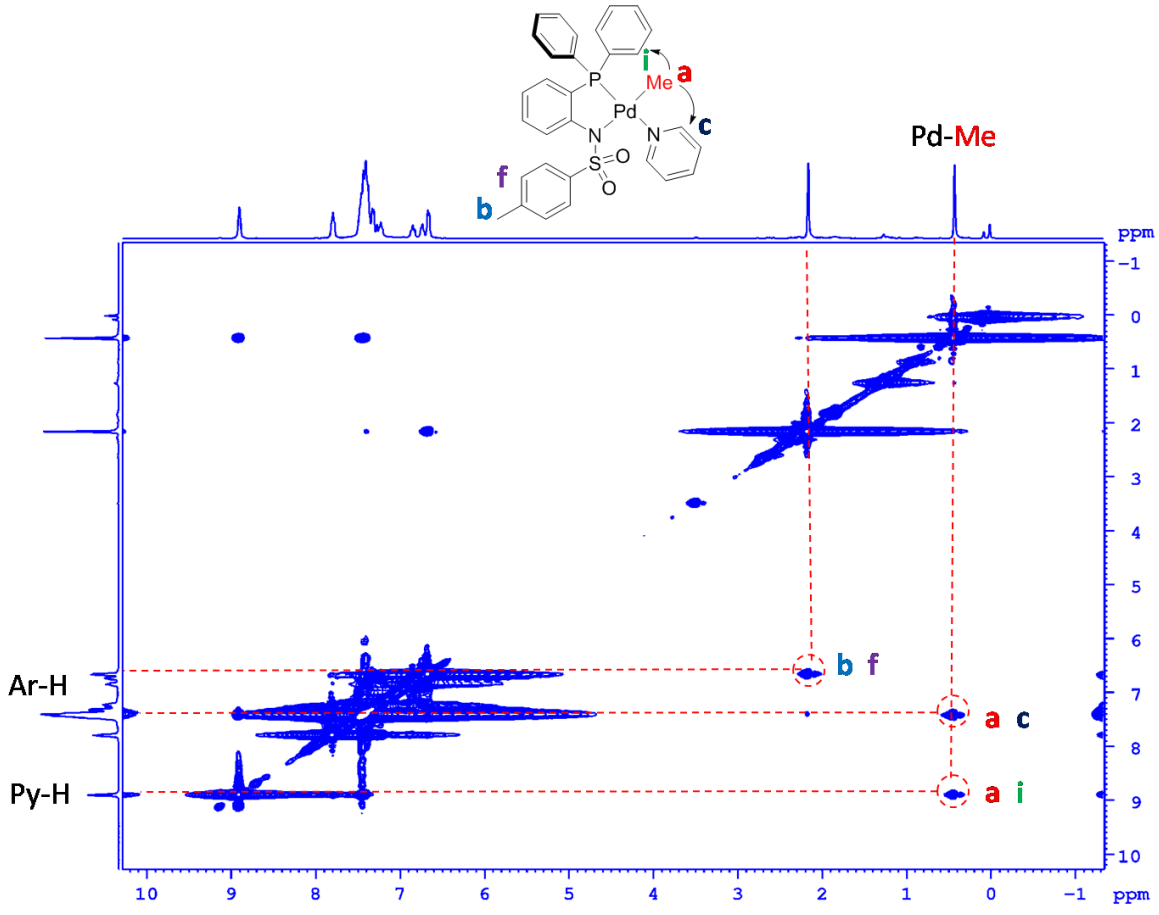



**Figure S40:** NOESY-NMR spectrum of complex **C2** in $CDCl_3$.

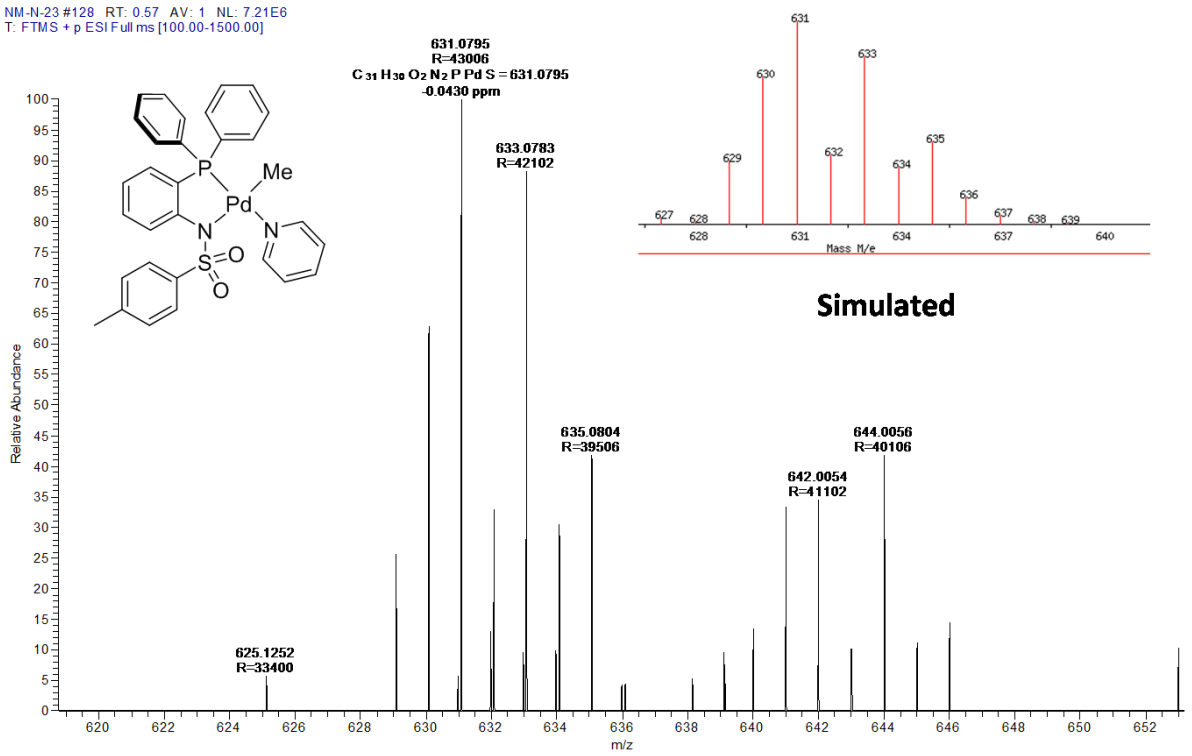



**Figure S41:** ESI-MS spectrum of complex **C2**.

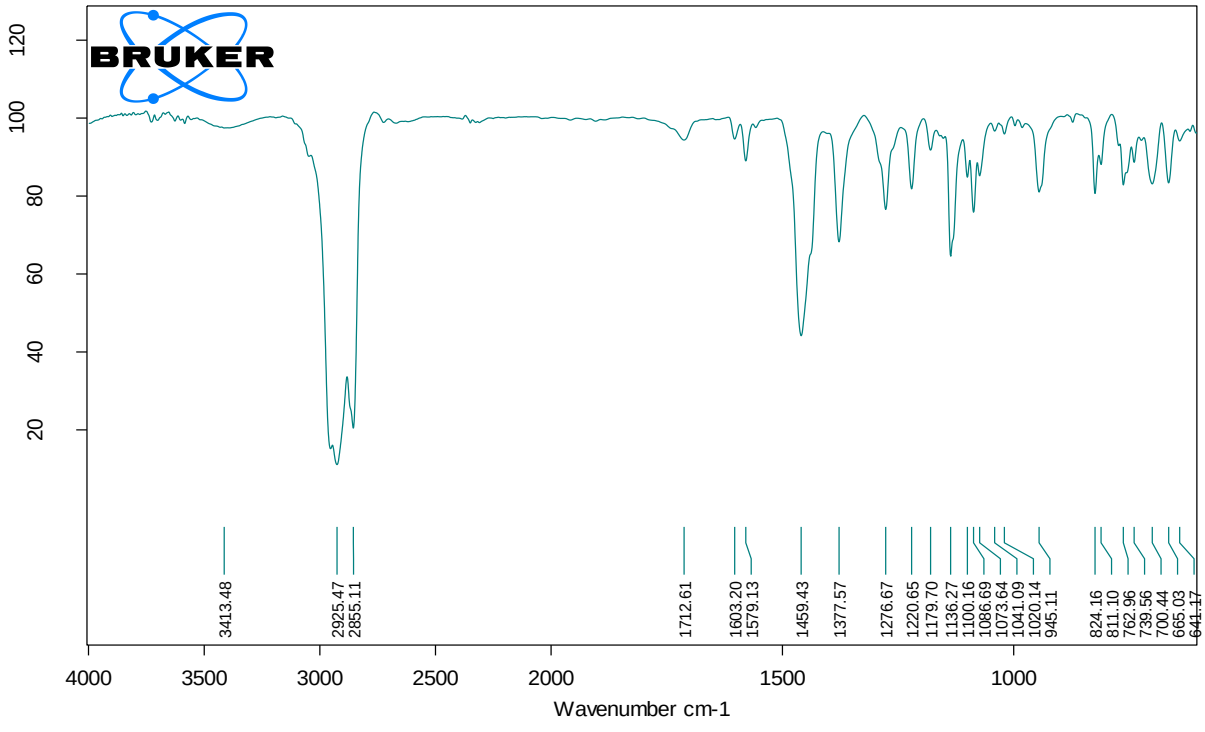



**Figure S42:** IR spectrum of complex **C2** in Nujol.

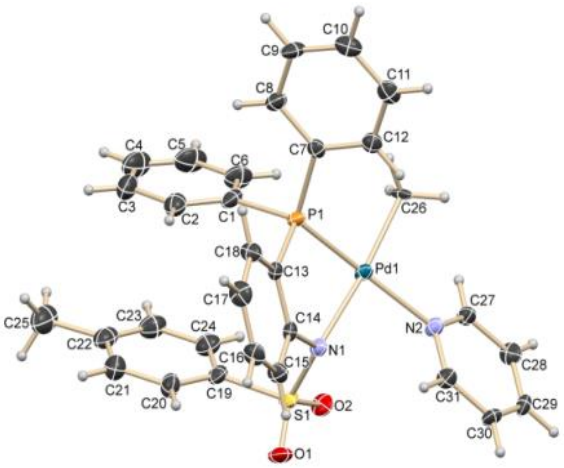


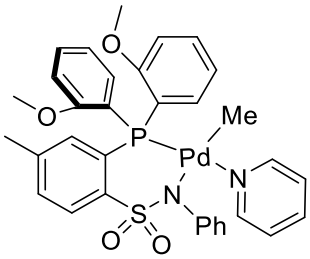

**Figure S43**: Molecular structure of complex **C2**.Thermal ellipsoids are drawn at 50% probability level.

**Table S4.** Crystal data and structure refinement for **C2**.

| | | |
|---|---|---|
| Identification code | **C2** | |
| Empirical formula | C62 H58 N4 O4 P2 Pd2 S2 | |
| Formula weight | 1261.98 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Triclinic | |
| Space group | P-1 | |
| Unit cell dimensions | a = 9.466(7) Å | α= 74.14(2)°. |
| | b = 13.978(11) Å | β= 87.92(2)°. |
| | c = 22.863(18) Å | γ = 85.66(2)°. |
| Volume | 2901(4) $Å^3$ | |
| Z | 2 | |
| Density (calculated) | 1.445 $Mg/m^3$ | |
| Absorption coefficient | 0.797 $mm^{-1}$ | |
| F(000) | 1288 | |
| Crystal size | 0.240 x 0.190 x 0.030 $mm^3$ | |
| Theta range for data collection | 2.334 to 25.195°. | |
| Index ranges | -11<=h<=11, -16<=k<=16, -27<=l<=27 | |
| Reflections collected | 30943 | |
| Independent reflections | 10372 [R(int) = 0.0727] | |
| Completeness to theta = 25.195° | 99.3 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.976 and 0.832 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |

| | |
|---|---|
| Data / restraints / parameters | 10372 / 0 / 689 |
| Goodness-of-fit on $F^2$ | 1.137 |
| Final R indices [I>2sigma(I)] | R1 = 0.0657, wR2 = 0.1566 |
| R indices (all data) | R1 = 0.0959, wR2 = 0.1679 |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 1.138 and -1.230 e.$Å^{-3}$ |

## 3.3. Palladium complex C3:




Equimolar mixture of ligand **L2A** and [(TMEDA)$PdMe_2$] was taken in a Schlenk tube and 8 mL pyridine was added. The content was stirred at room temperature for 3 hours and the volatiles were evaporated. Subsequently, pyridine (8 mL) was added, mixture was stirred and volatiles were evaporated. This procedure was repeated for 2 more times and the resultant solid was dried under vacuum for 4 hours. The desired complex was obtained in 92 % yield after washing with diethyl ether and drying. Crystal suitable for single crystal X-ray analysis were obtained by slow evaporation of DCM solution of **C3**.

**$^{31}$P NMR** (500 MHz in $CDCl_3$): δ = 22.86. **$^{1}$HNMR** (500 MHz in $CDCl_3$): δ = 8.85 (s, 2H), 7.89 (s, 1H), 7.68 (s, 1H), 7.50 (s, 2H), 7.27-7.29 (m, 5H), 7.13-7.20 (m, 3H), 7.15 (s, 2H), 6.89 (s, 5H), 6.67 (s, 1H), 3.35 (s, 6H *o*-OMe), 2.25 (s, 3H *p*-Me), 0.04 (s, 3H Pd-Me).

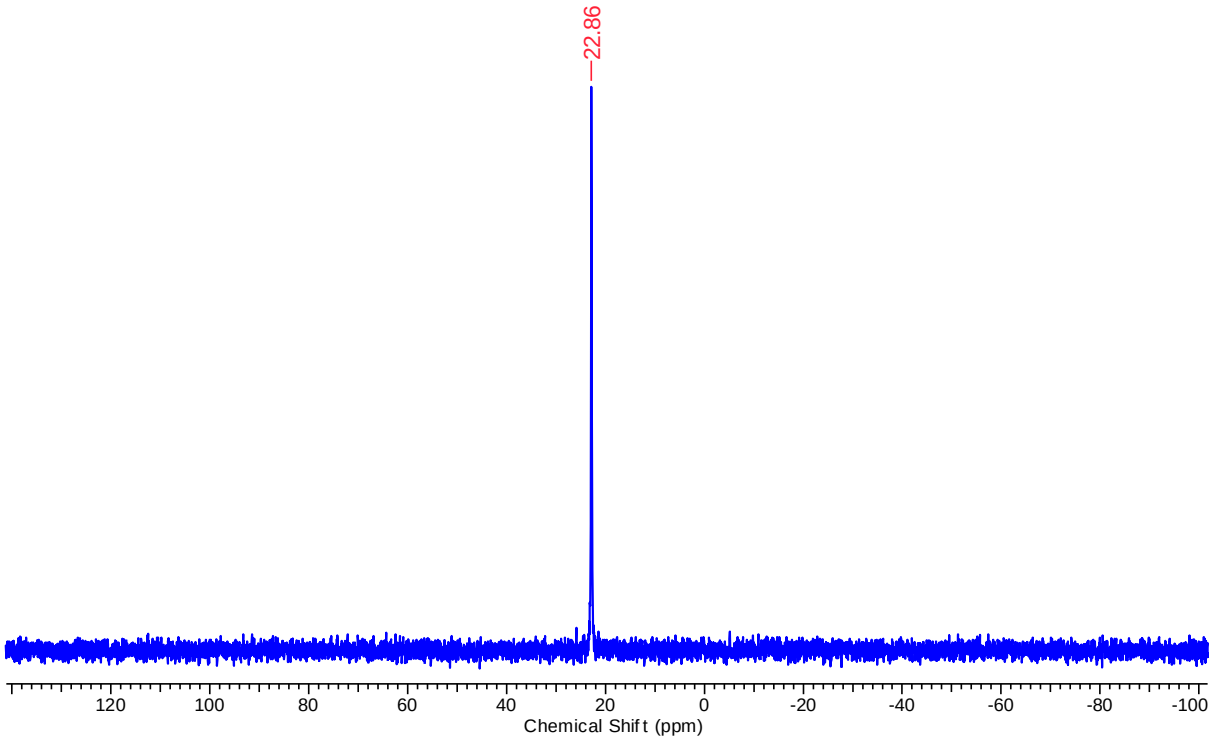



**Figure S44:** $^{31}P$ NMR spectrum of complex **C3** in $CDCl_3$.

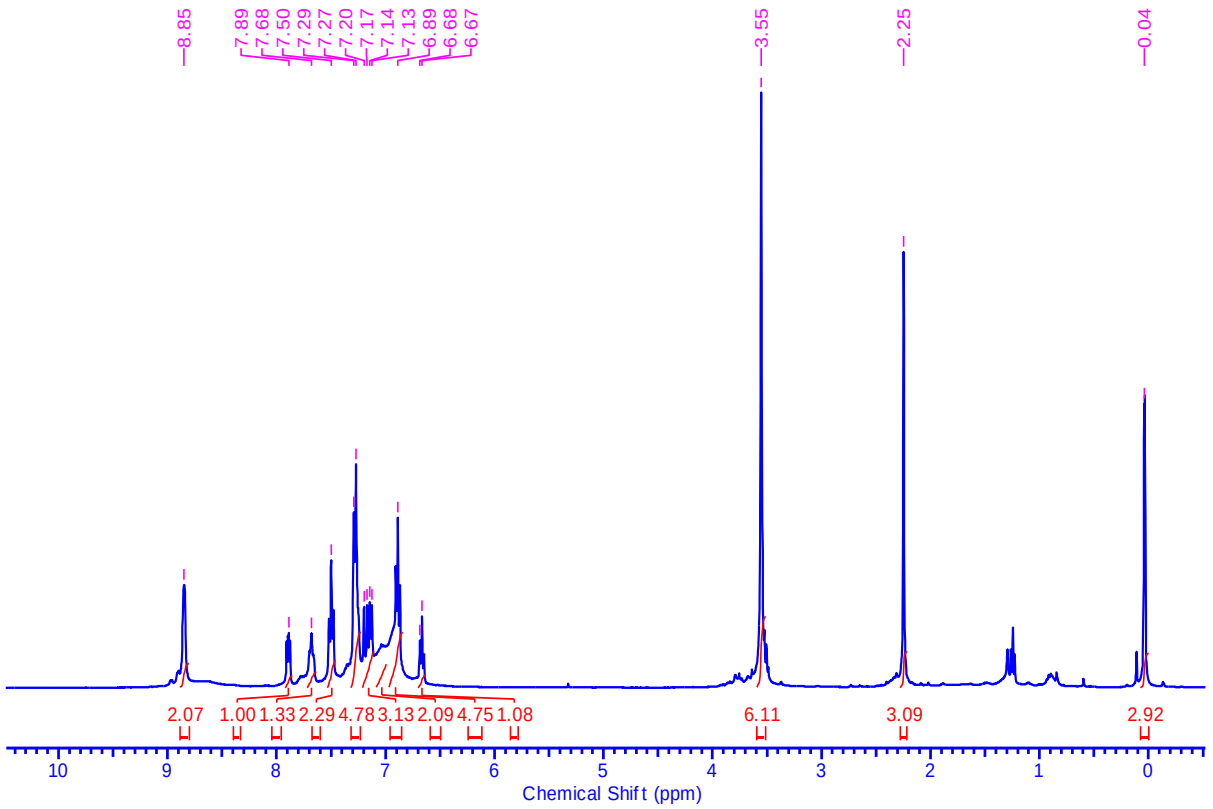



**Figure S45:** $^{1}H$ NMR spectrum of complex **C3** in $CDCl_3$.

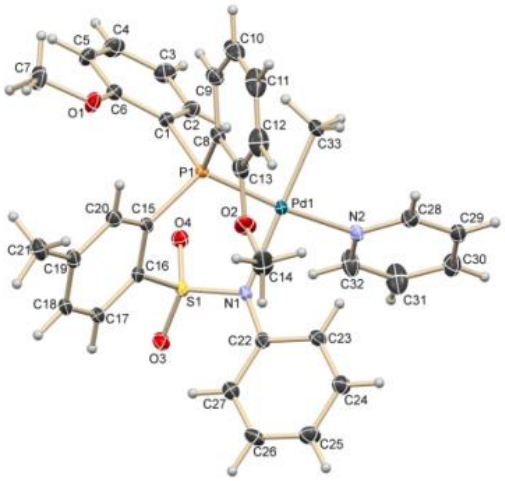


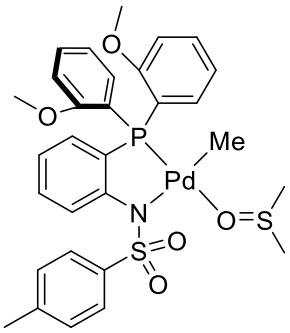

**Figure S46:** Molecular structure of complex **C3**. Thermal ellipsoids are drawn at 50% probability level.

**Table S5.** Crystal data and structure refinement for **C3**.

| | | |
|---|---|---|
| Identification code | **C3** | |
| Empirical formula | C33 H33 N2 O4 P Pd S | |
| Formula weight | 691.04 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Triclinic | |
| Space group | P-1 | |
| Unit cell dimensions | a = 9.959(2) Å | α= 91.745(8)°. |
| | b = 11.496(3) Å | β= 100.761(8)°. |
| | c = 13.574(3) Å | γ = 95.062(9)°. |
| Volume | 1519.0(6) $Å^3$ | |
| Z | 2 | |
| Density (calculated) | 1.511 $Mg/m^3$ | |
| Absorption coefficient | 0.773 $mm^{-1}$ | |
| F(000) | 708 | |
| Crystal size | 0.200 x 0.170 x 0.030 $mm^3$ | |
| Theta range for data collection | 2.614 to 27.997°. | |
| Index ranges | -13<=h<=13, -15<=k<=15, -17<=l<=17 | |
| Reflections collected | 50137 | |
| Independent reflections | 7286 [R(int) = 0.0510] | |
| Completeness to theta = 25.242° | 99.6 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.977 and 0.861 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |

| | |
|---|---|
| Data / restraints / parameters | 7286 / 0 / 383 |
| Goodness-of-fit on $F^2$ | 1.062 |
| Final R indices [I>2sigma(I)] | R1 = 0.0273, wR2 = 0.0689 |
| R indices (all data) | R1 = 0.0318, wR2 = 0.0720 |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 1.065 and -0.631 e.Å$^{-3}$ |

## 3.4. Palladium complex C4:




Sodium salt of ligand **L1A** (0.100 gm, 0.198 mmol) and [(COD)PdMeCl] (0.052g, 0.198 mmol) were mixed in a Schlenk tube and 6 mL DCM was added along with 10 equivalent of DMSO. The content was stirred at room temperature for 2 hours and then passed through a bed of celite. Solvent was evaporated and the residue was washed with hexane. The resultant gray solid was dried for 2 to 3 hours under vacuum to obtain **C4** in 66 % isolated yield.

**$^{31}$P NMR** (500 MHz in $CDCl_3$): δ = 25.07. **$^{1}$H NMR** (500 MHz in $CDCl_3$): δ = 7.61 (s, 1H, Ar-H). 7.42 (s, 3H, Ar-H), 7.11 (s, 3H, Ar-H), 6.88 (s, 3H, Ar-H), 6.76 (m, 5H, Ar-H), 6.62 (s, 1H, Ar-H), 3.65 (s, 6H, *o*-OMe), 2.70 (s, $SMe_2$ Excess of DMSO present), 2.18 (s, 3H, *p*-Me), 0.55 (s, 3H, Pd-Me). **$^{13}$C NMR** (125 MHz in $CDCl_3$): δ = 160.5,153.3, 143, 139.7, 134.9, 132.3, 131.5, 129.2, 128.8, 128.4, 126.8, 121.3, 120.8, 120.6, 120.5, 120.1, 111.1, 55.4, 41.79, 21.19, -0.8. **ESI-MS:** Calculated *m/z* for$[C_{28}H_{29}O_4NPPdS]^+$= 612.0584 $[M\text{-}DMSO+H]^+$; found *m/z* = 612.0586 $[M\text{-}DMSO+H]^+$.

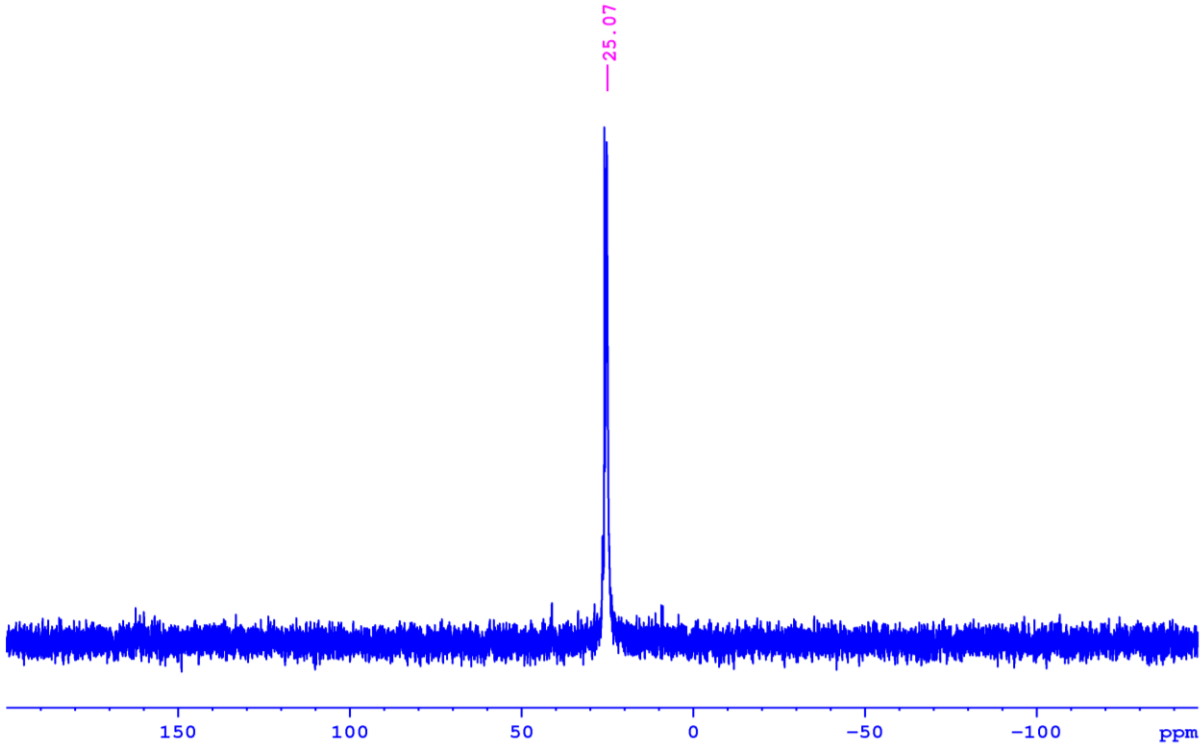



**Figure S47:** $^{31}P$ NMR spectrum of complex **C4** in $CDCl_3$.

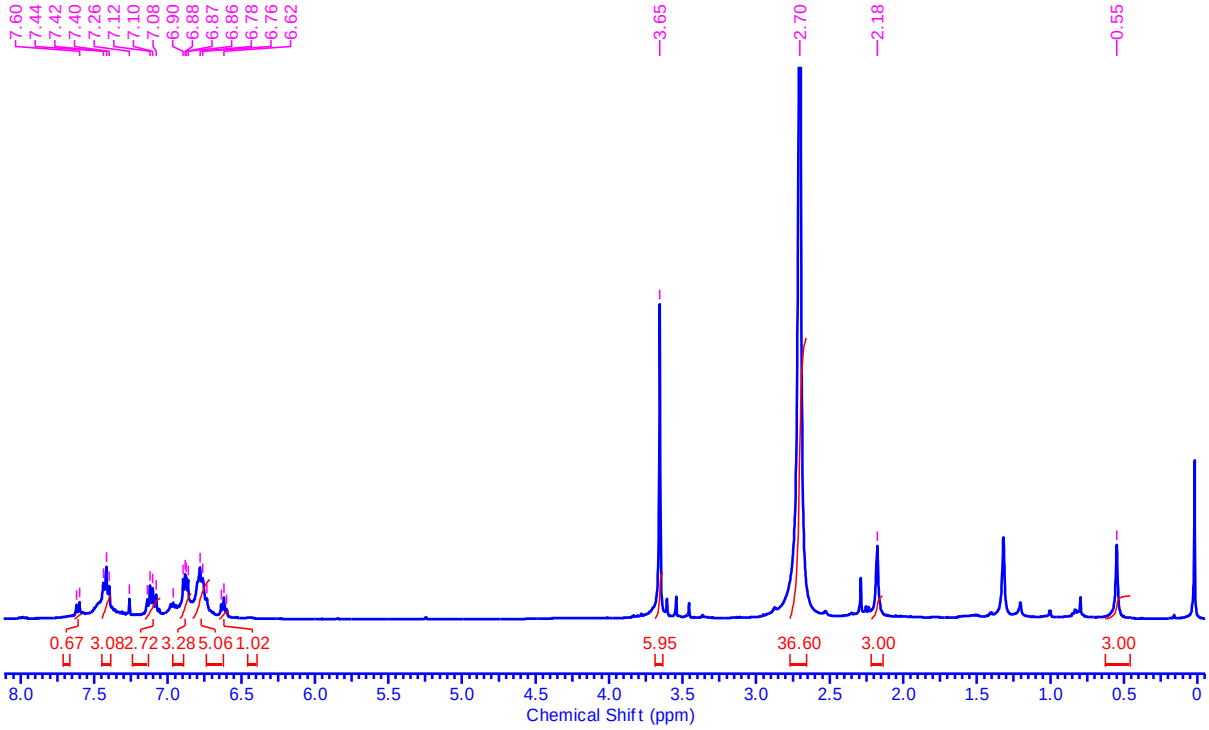



**Figure S48:** $^{1}H$ NMR spectrum of complex **C4** in $CDCl_3$.

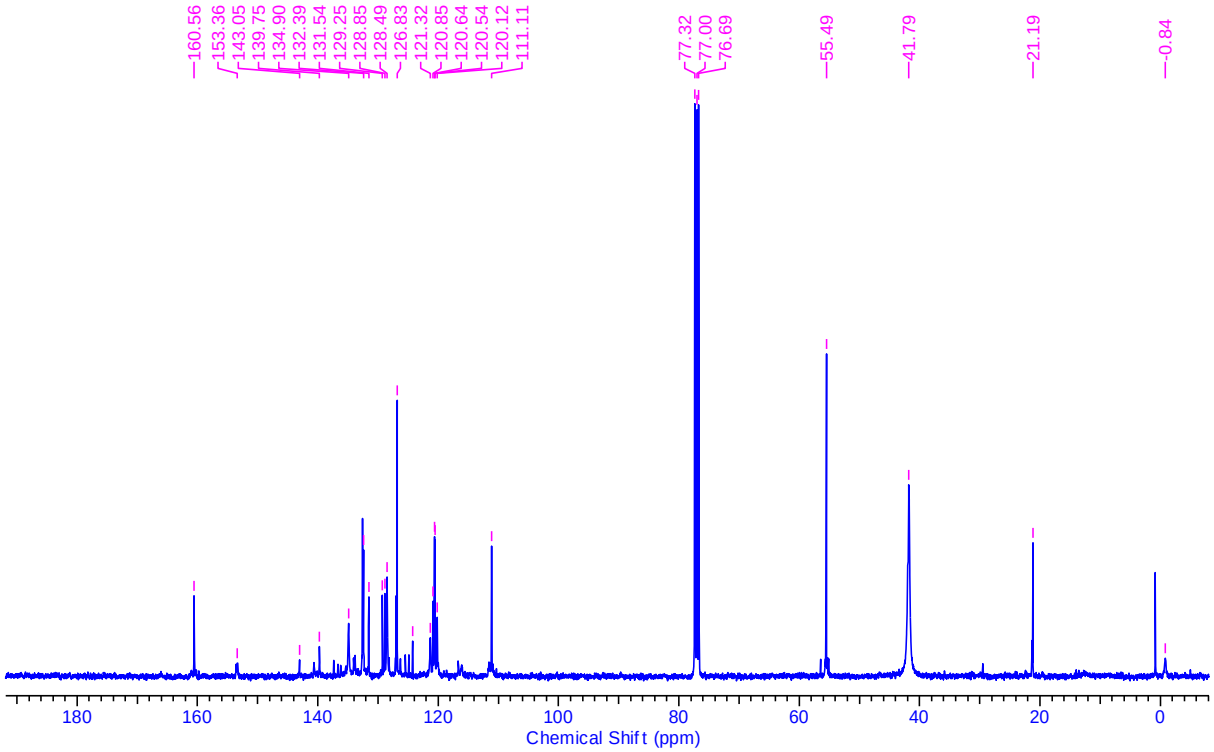



**Figure S49:** $^{13}C$ NMR spectrum of complex **C4** in $CDCl_3$.

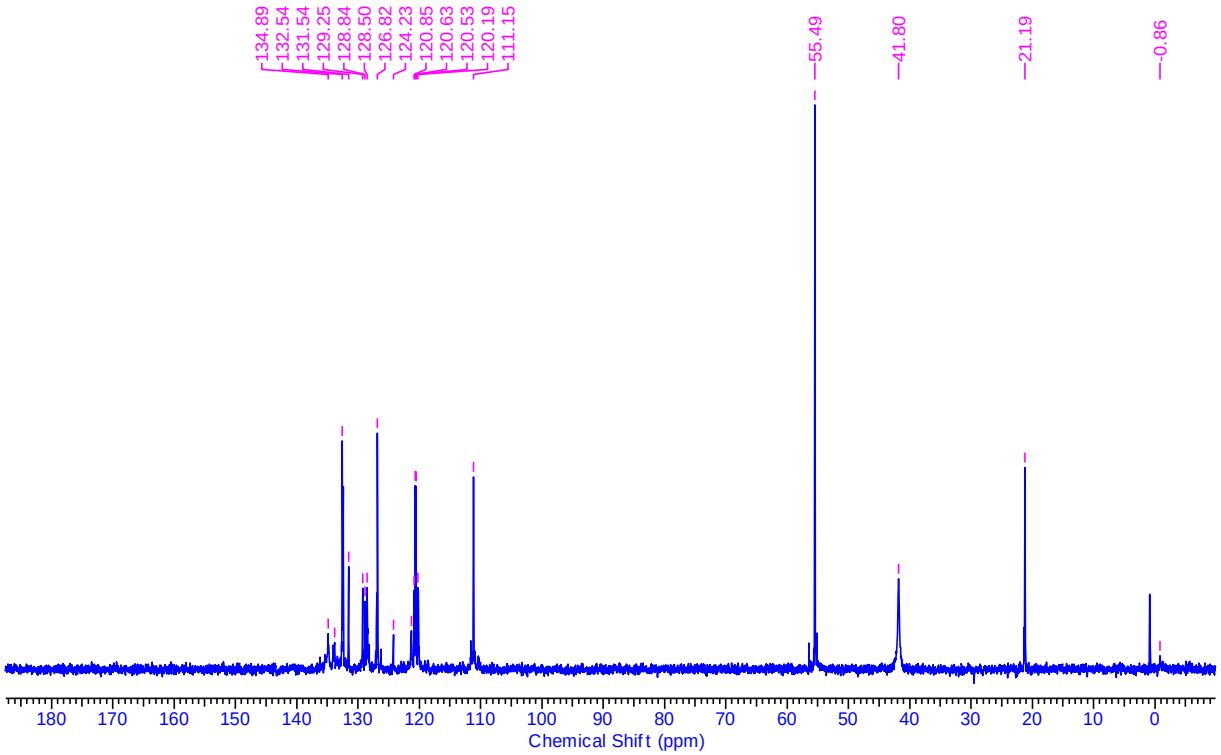



**Figure S50:** DEPT-NMR spectrum of complex **C4** in $CDCl_3$.

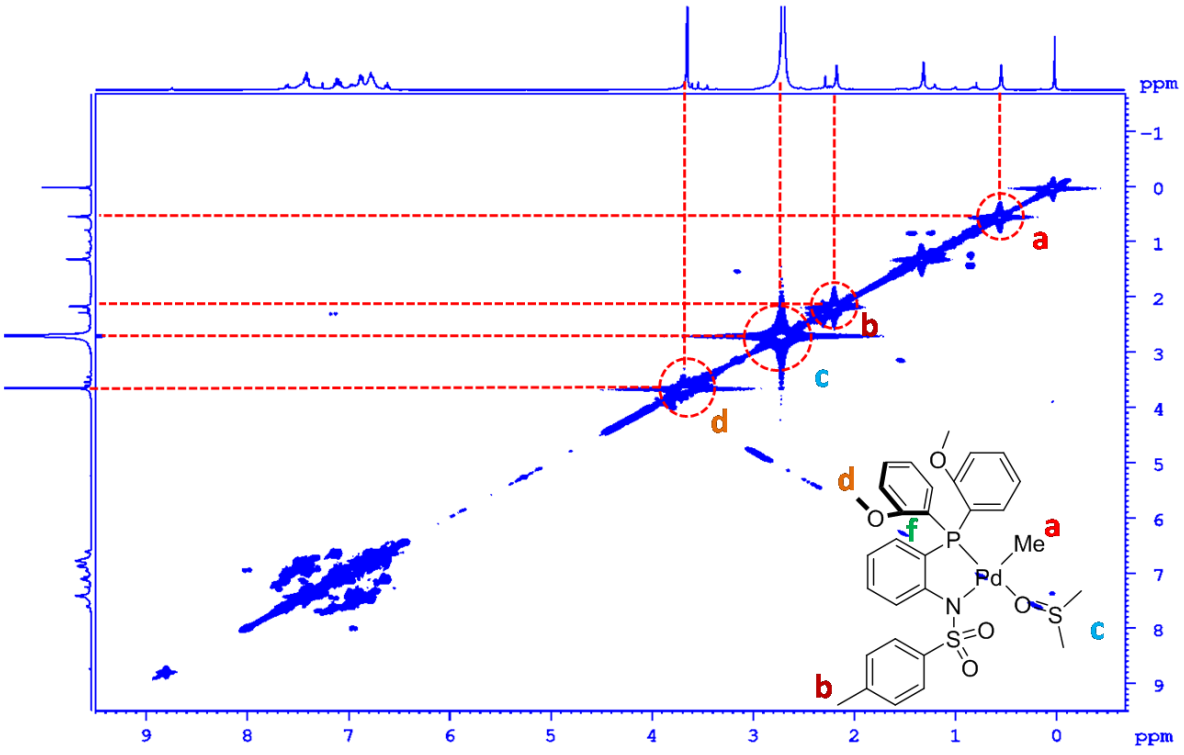



**Figure S51:** COSY-NMR spectrum of complex **C4** in $CDCl_3$.

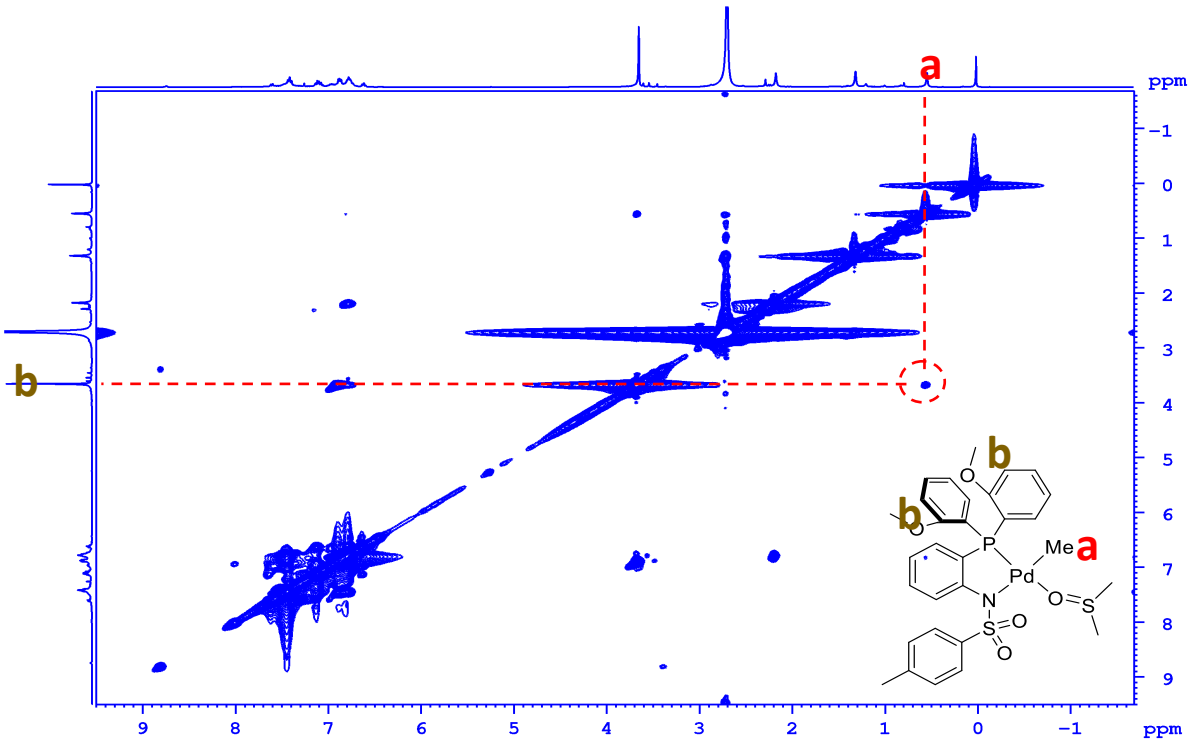



**Figure S52:** NOESY-NMR spectrum of complex **C4** in $CDCl_3$.

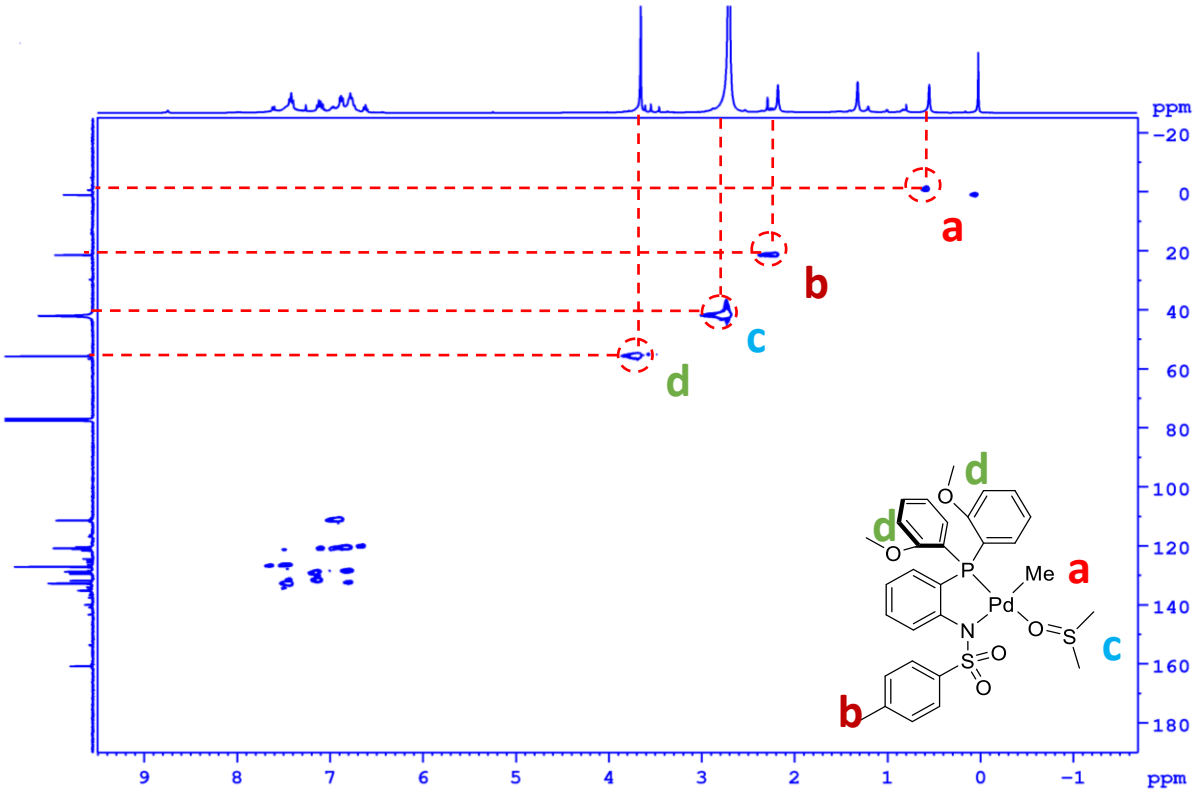



**Figure S53:** HSQC-NMR spectrum of complex **C4** in $CDCl_3$.

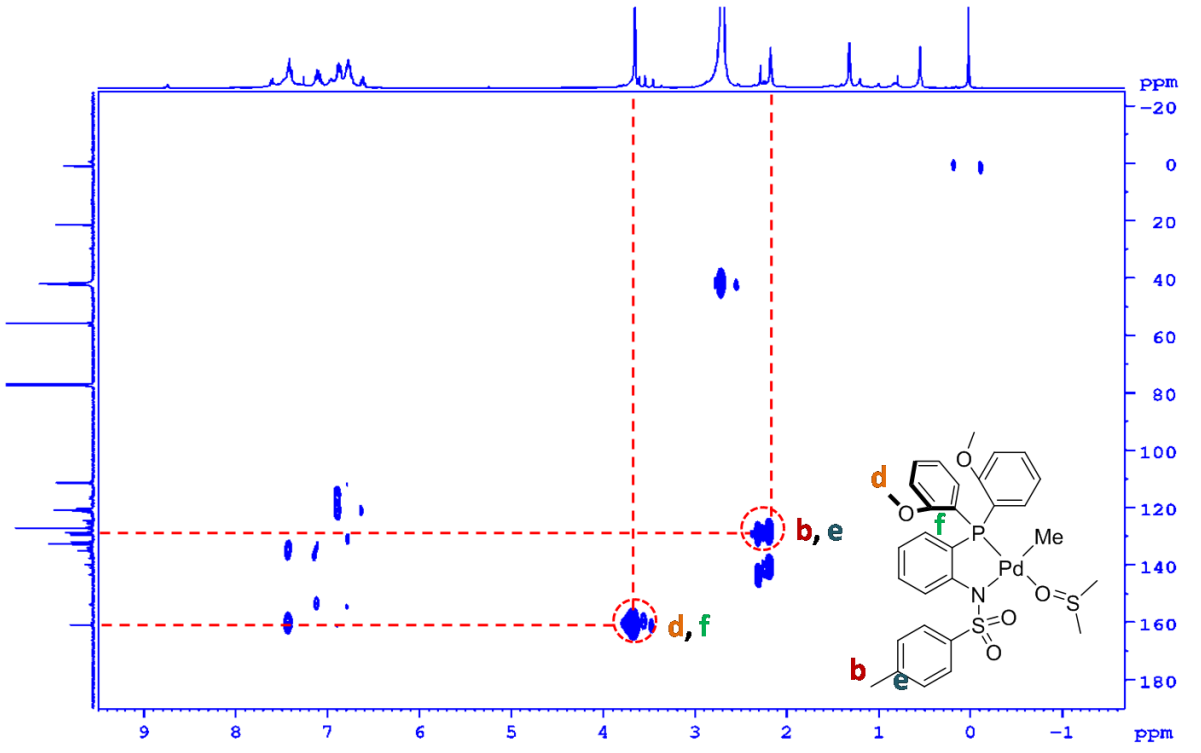



**Figure S54:** HMBC-NMR spectrum of complex **C4** in $CDCl_3$.

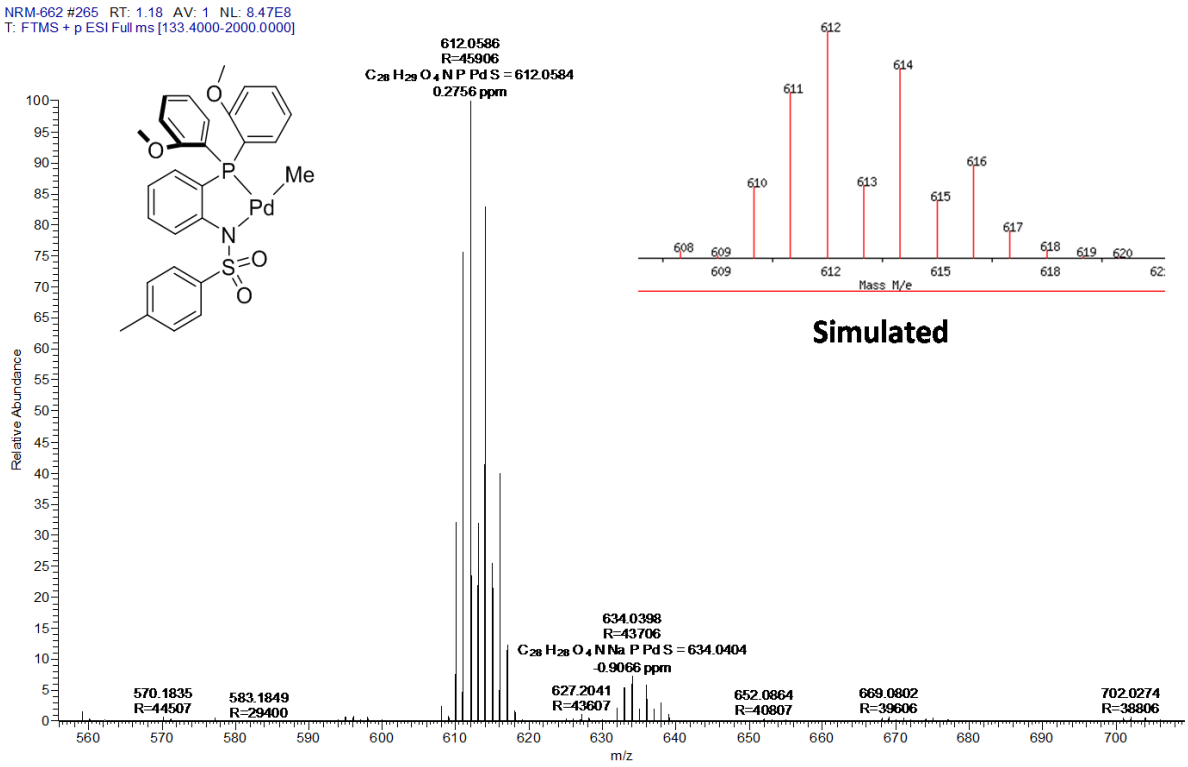
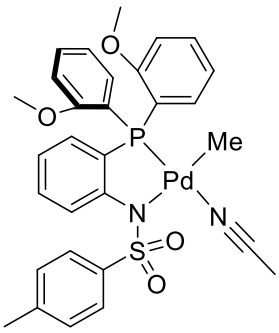



**Figure S55:** ESI-MS spectrum of complex **C4**.

## 3.5. Palladium complex C5:




Sodium salt of ligand **L1A** (0.250 gm, 0.48 mmol) and [(COD)PdMeCl] (0.129 gm, 0.48 mmol) was stirred at room temperature in acetonitrile (10 mL) for 10 minutes. $AgBF_4$ (0.094 gm, 0.48 mmol) was added in reaction mixture and the mixture was stirred for 10 minutes. Reaction mixture was passed through a bed of celite. After the evaporation of solvent, off white solid was obtained in 74 % isolated yield.

**$^{31}$P NMR** (500 MHz in $CDCl_3$): δ = 29.01. **$^{1}$H NMR** (500 MHz in $CDCl_3$): δ = 7.6 (s, 1H, Ar-H), 7.52 (s, 2H, Ar-H), 7.44 (s, 2H, Ar-H), 7.10 (s, 1H, Ar-H), 7.02 (s, 2H, Ar-H), 6.83-6.89 (m, 7H, Ar-H), 6.57, (s, 1H, Ar-H), 3.66 (s, 6H, *o*-OMe), 2.22 (s, 3H, *p*-Me), 2.10 (s, 3H, MeCN), 0.35 (s, 3H, Pd-Me). **$^{13}$C NMR** (125 MHz in $CDCl_3$): δ = 160.7, 160.6, 141, 140, 135.4, 132.4, 132.1, 131.6, 128.4, 127, 123.8, 121, 120.6, 120.5, 119.1, 117.2, 111.1, 55.50,

31, 27.6, 21.3, -4.9. **ESI-MS:** Calculated *m/z* for$[C_{28}H_{29}NO_4PPdS]^+$= 612.0584 [M-MeCN+H]$^+$; found *m/z* = 612.0587 [M-MeCN+H]$^+$.

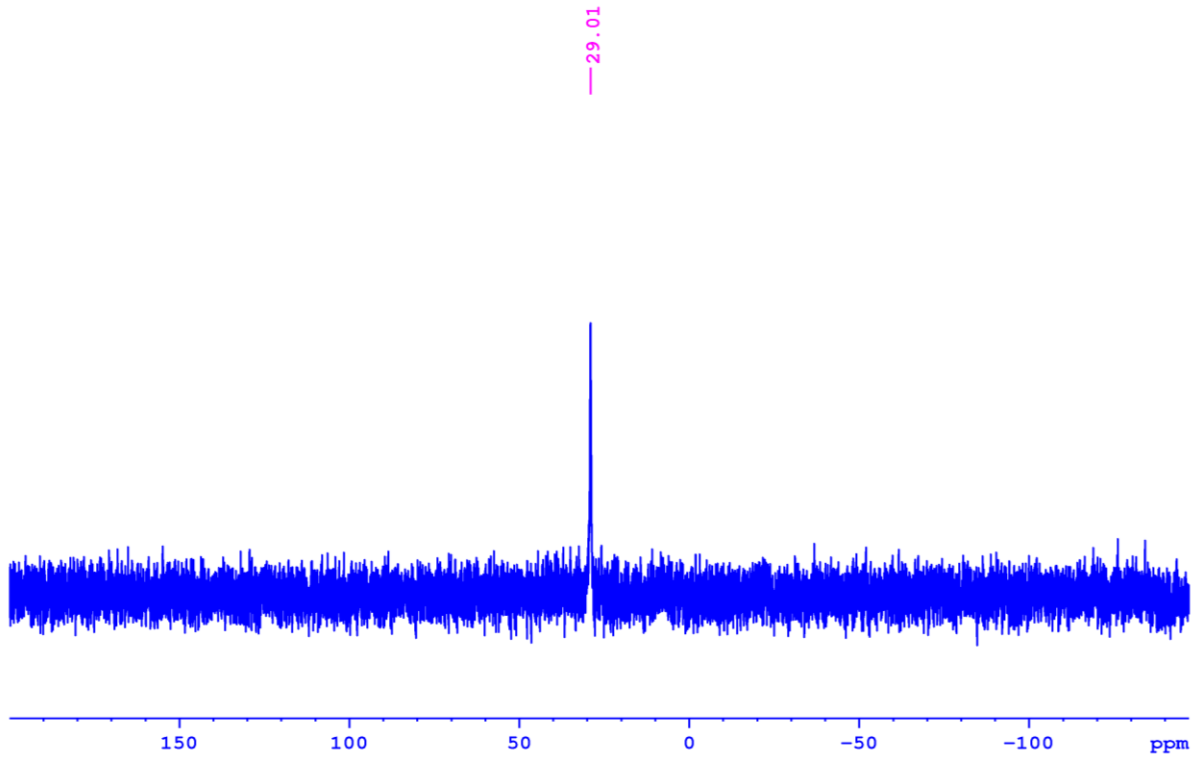



**Figure S56:** $^{31}$P NMR spectrum of complex **C5** in $CDCl_3$.

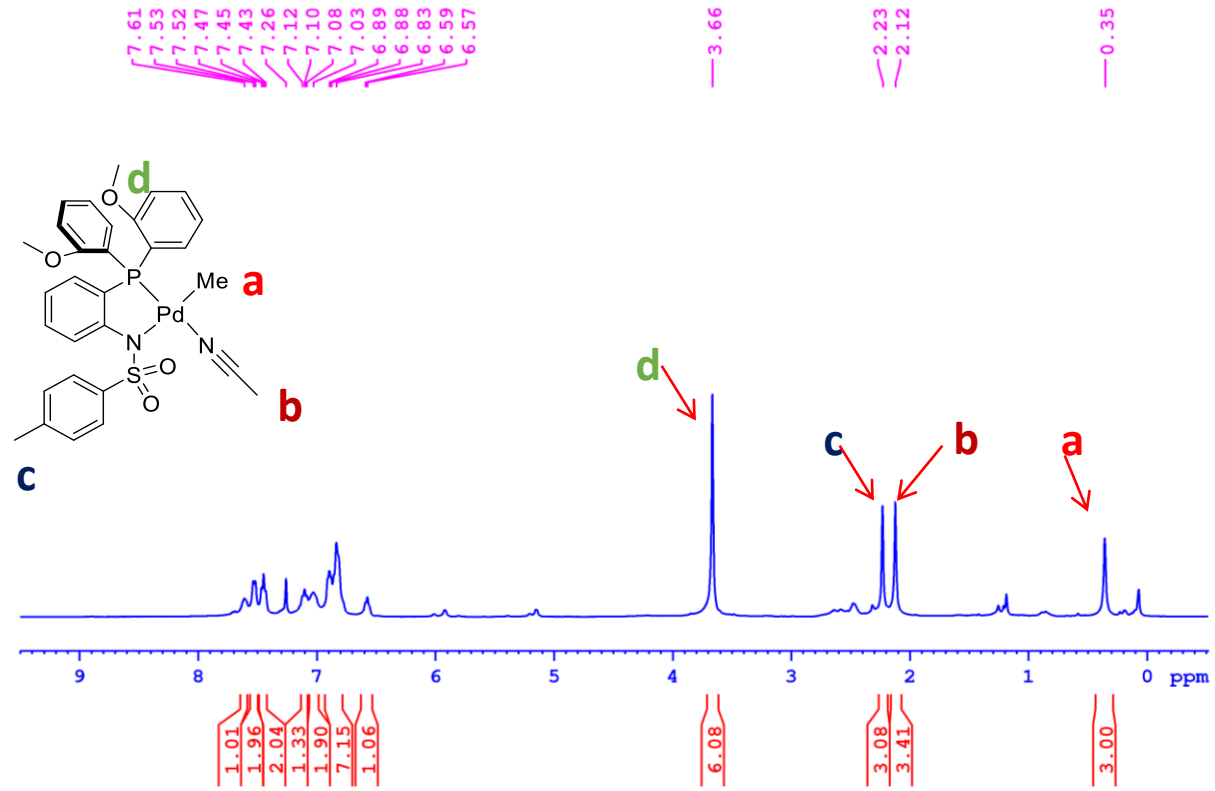



**Figure S57:** $^1$H NMR spectrum of complex **C5** in $CDCl_3$.

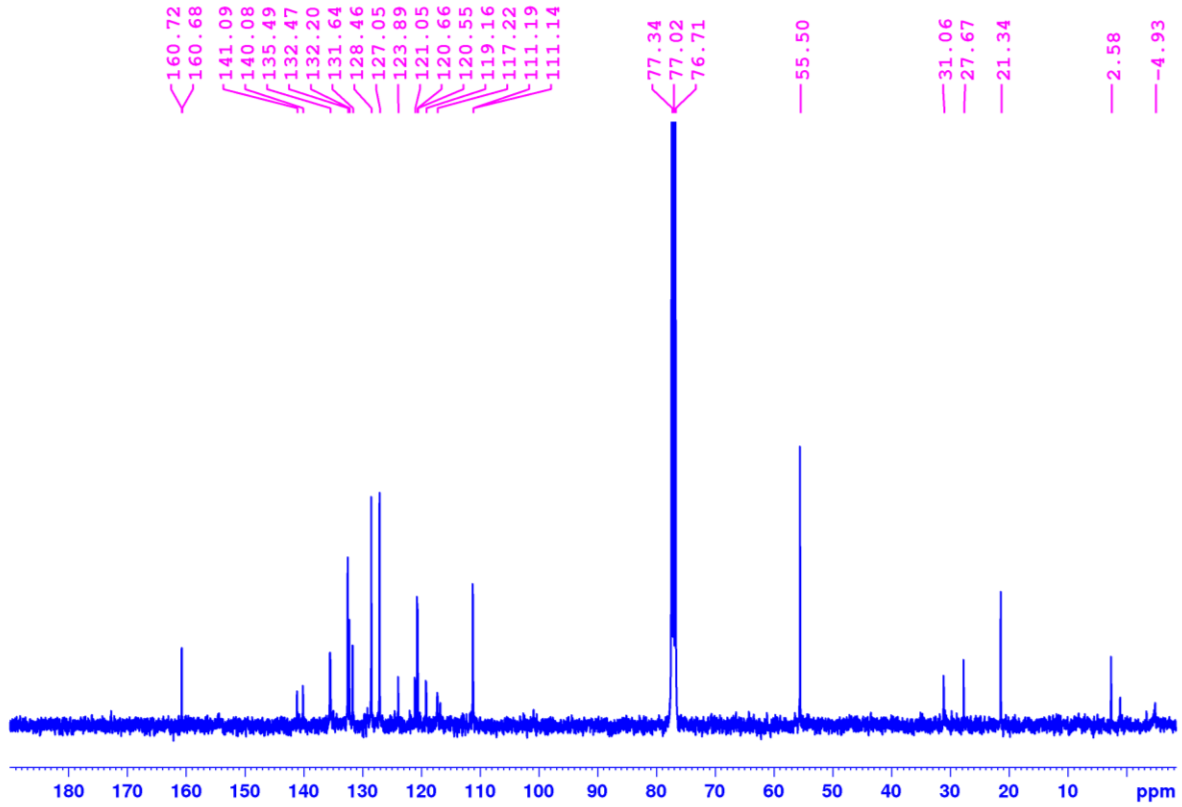



**Figure S58:** $^{13}$CNMR spectrum of complex **C5** in $CDCl_3$.

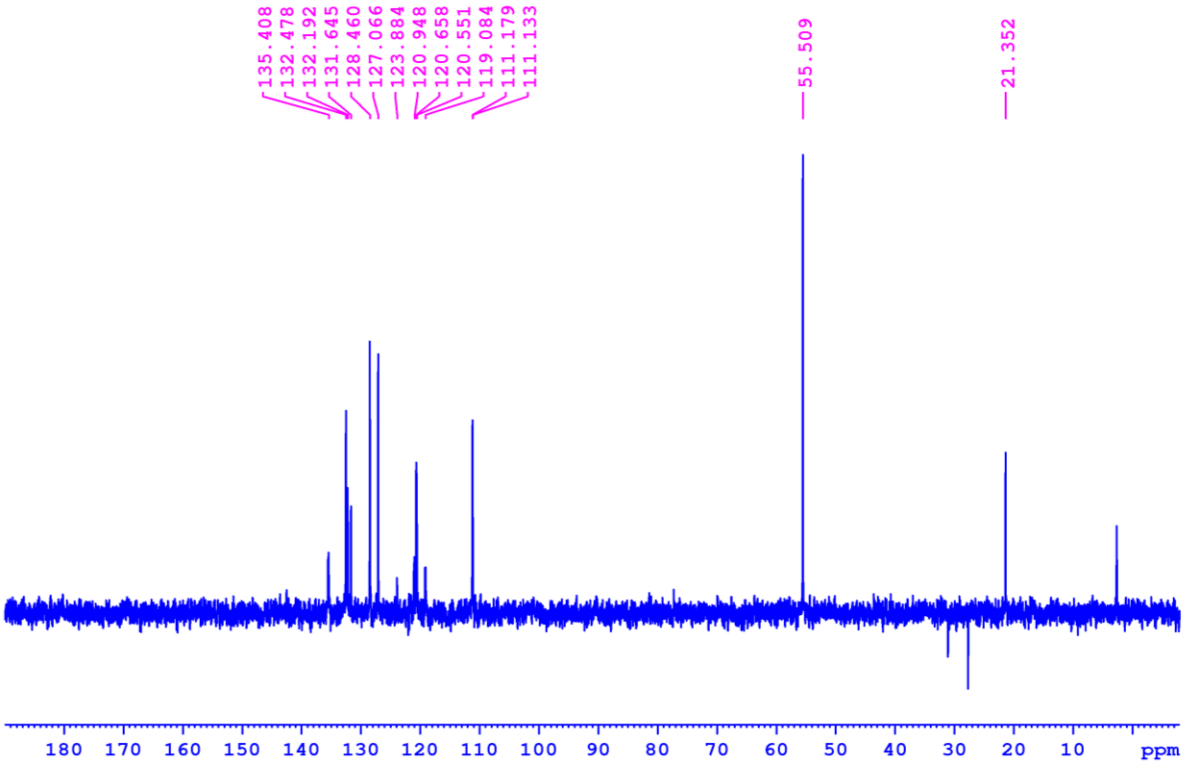



**Figure S59:** DEPT-NMR spectrum of complex **C5** in $CDCl_3$.

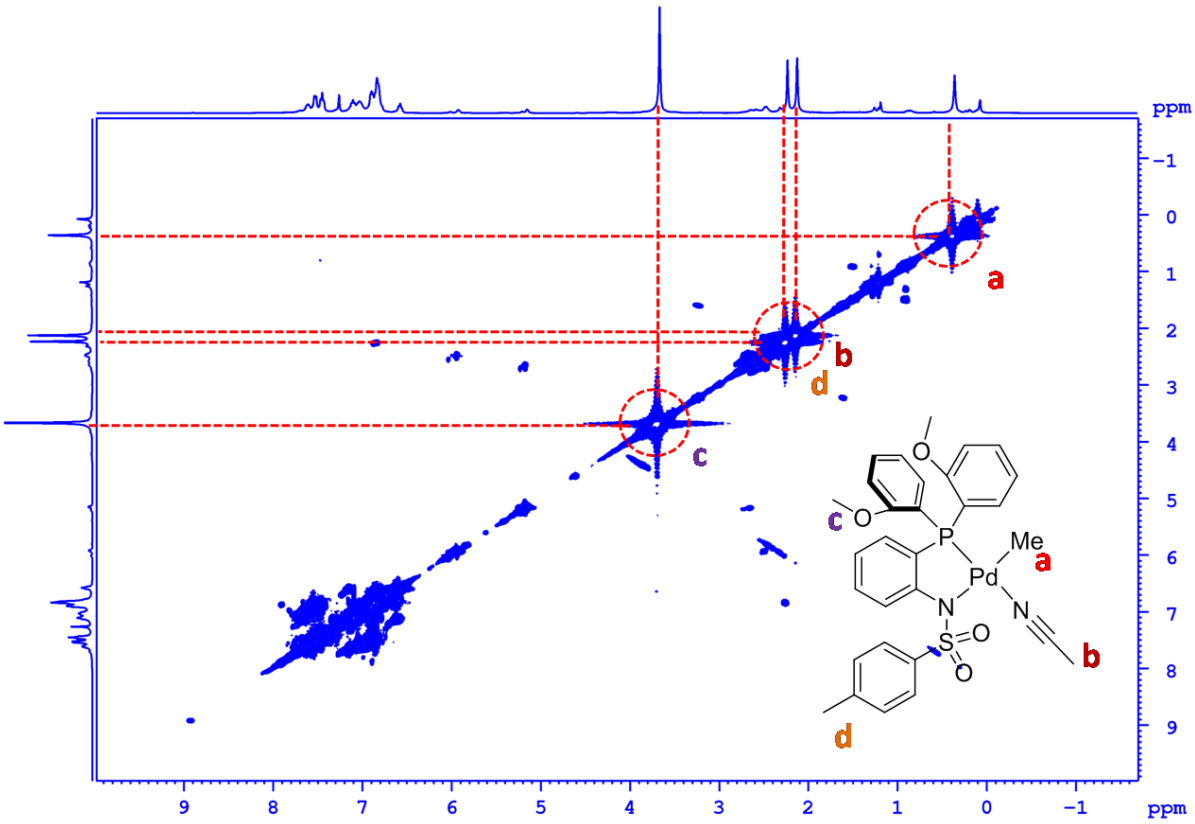



**Figure S60:** COSY-NMR spectrum of complex **C5** in $CDCl_3$.

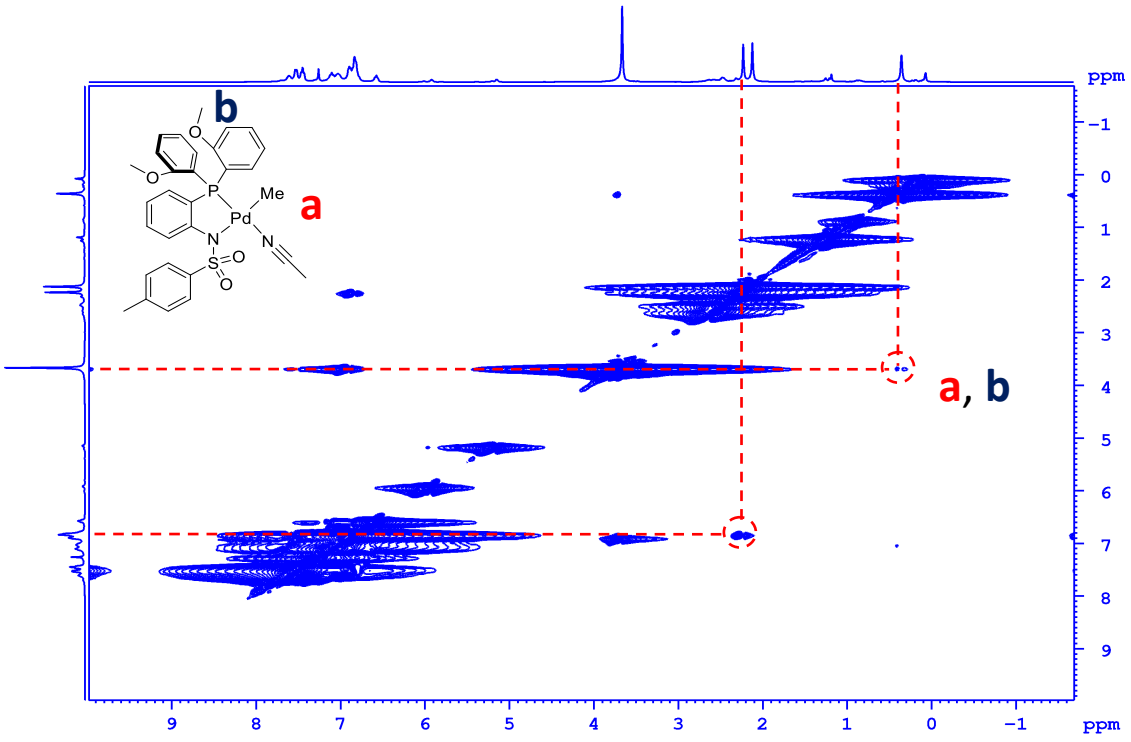



**Figure S61:** NOESY-NMR spectrum of complex **C5** in $CDCl_3$.

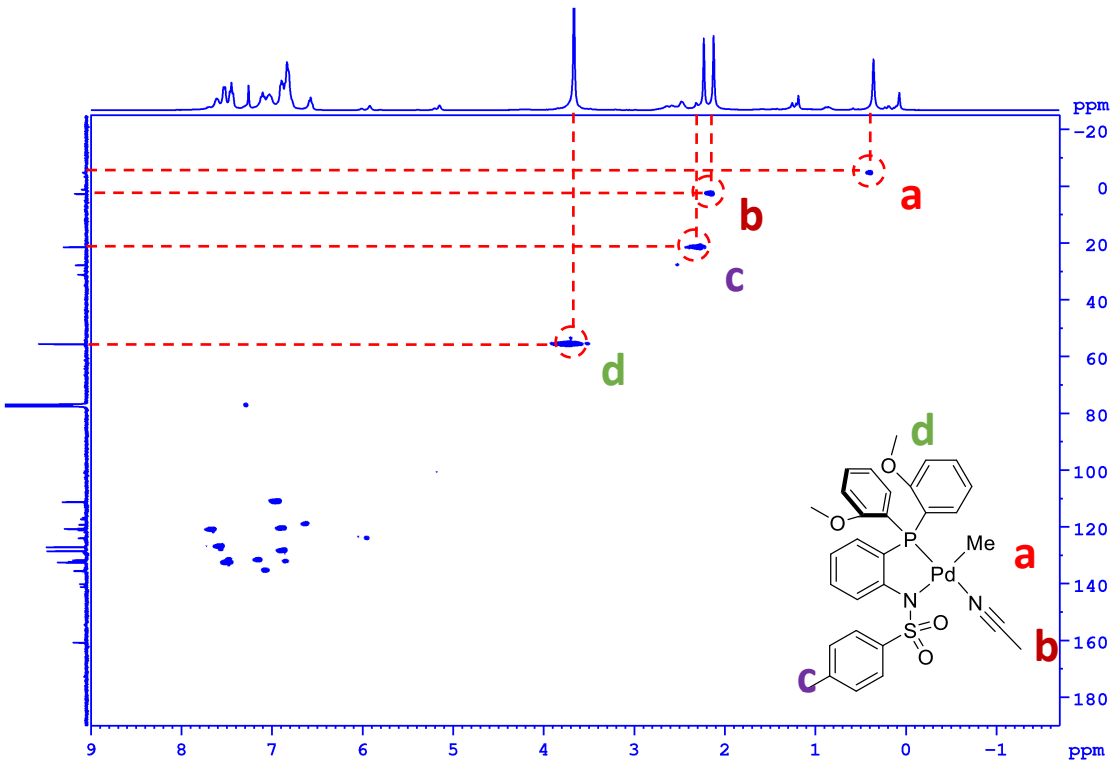



**Figure S62:** HSQC-NMR spectrum of complex **C5** in $CDCl_3$.

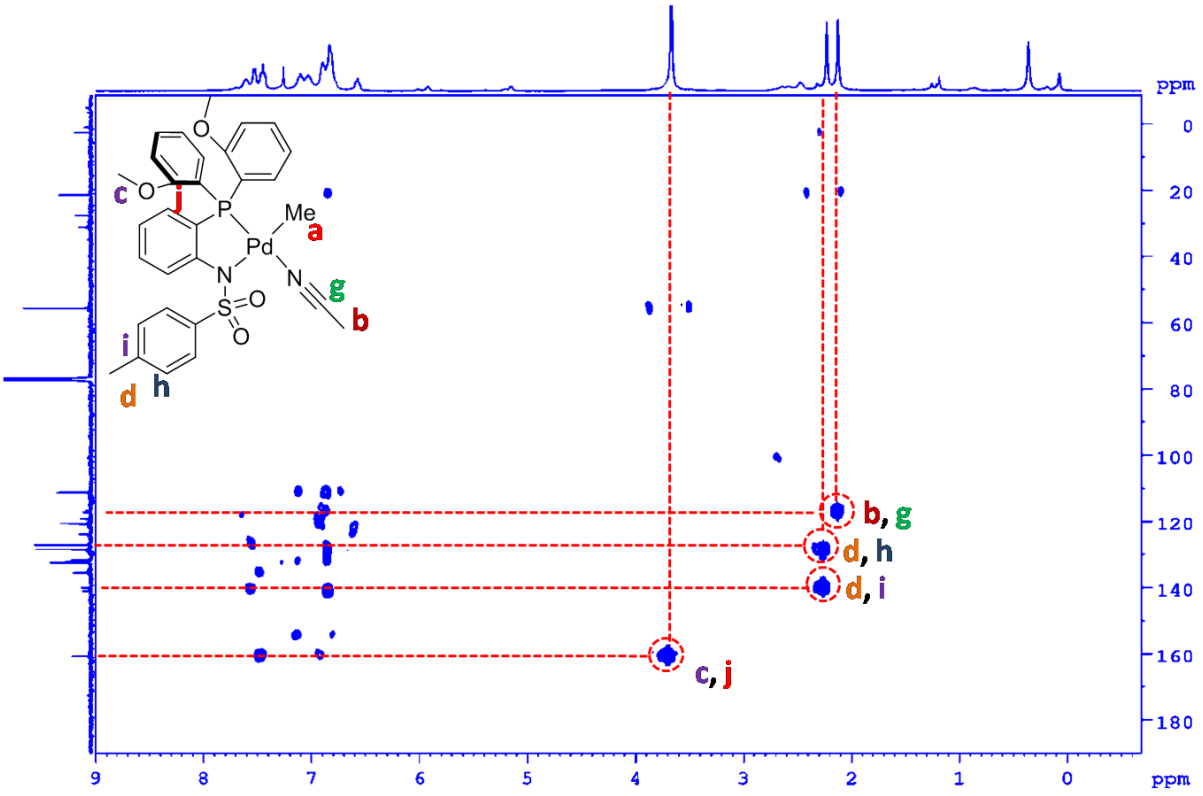



**Figure S63:** Long-range C-H correlation (HMBC) NMR spectrum of complex **C5** in $CDCl_3$.

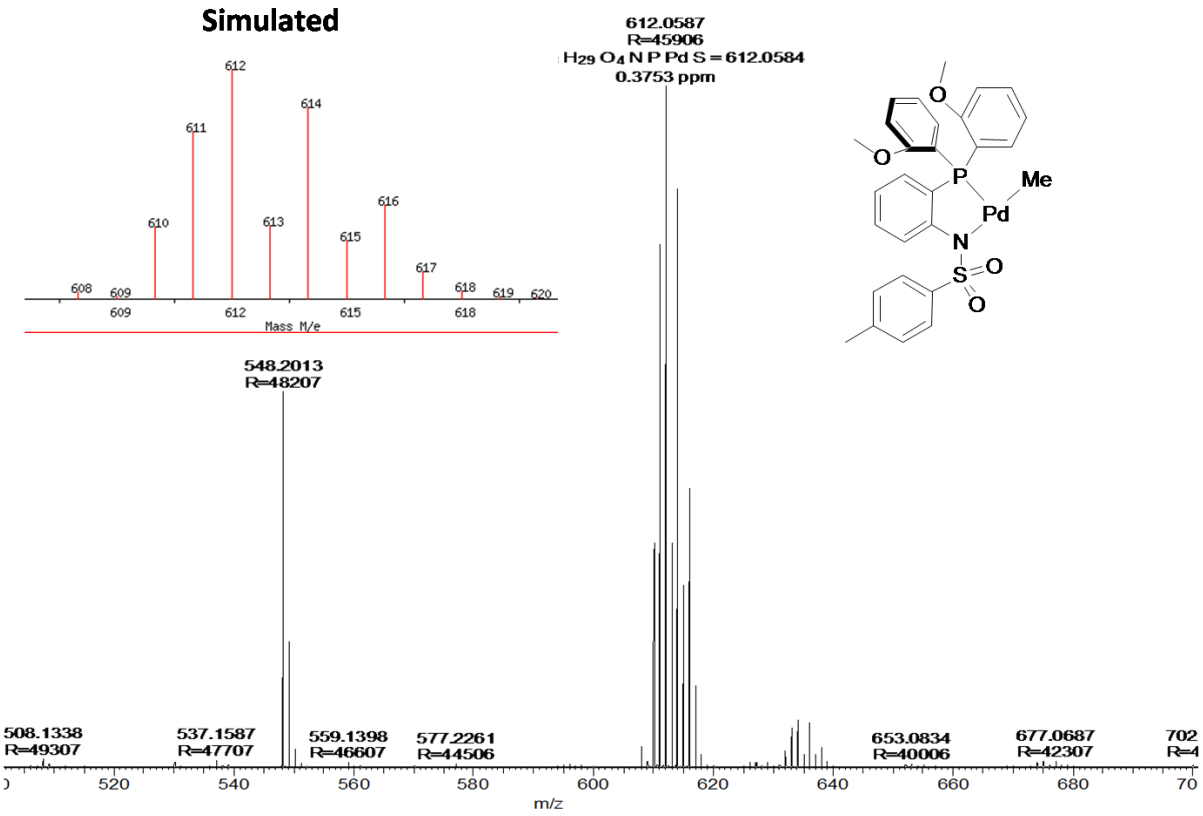



**Figure S64:** ESI-MS spectrum of complex **C5** in acetonitrile.

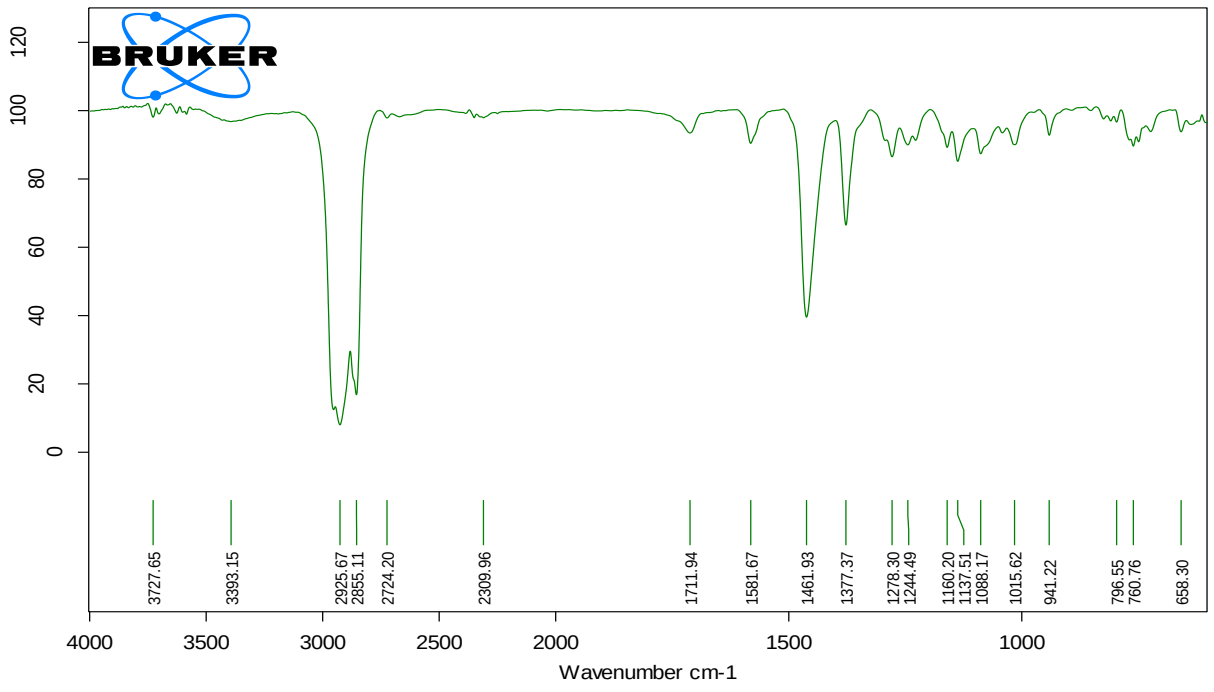
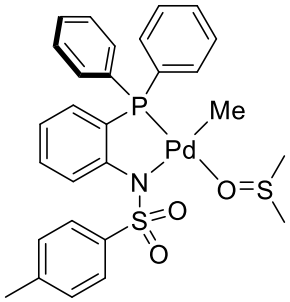



**Figure S65:** IR spectrum of complex **C5** in Nujol.

## 3.6. Palladium complex C6:




Ligand **L1B** (0.183 gm, 0.42 mmol) was treated with sodium hydride (0.011 gm, 0.50 mmol) in THF (6 mL) for 24 hours at room temperature. After evaporation of THF, the sodium salt of ligand **L1B** was suspended in DCM (12 mL) and $[(DMSO)PdMeCl]_2$ (0.100 gm, 0.42 mmol) was added. The reaction mixture was stirred at room temperature for 3 hours. Resulting gray solution was passed through a bed of celite under argon. Volatiles were evaporated in vacuum and the resultant residue was dried for 3 hours. The thus obtained residue was washed with hexane to obtain palladium complex in 70 % yield.

**$^{31}$P NMR** (400 MHz in $CDCl_3$): δ = 40.64. **$^{1}$H NMR** (400 MHz in $CDCl_3$): δ = 7.57 (s, 2H, Ar-H). 7.38-7.44 (m, 10H, Ar-H), 7.26 (s, 2H, Ar-H), 7.18 (s, 1H, Ar-H), 6.61 (m, 3H, Ar-H), 2.73 (s, 6H, $SMe_2$ excess of DMSO was observed), 2.22 (s, 3H, *p*-Me), 0.56 (s, 3H, Pd-Me). **ESI-MS:** Calculated *m/z* for$[C_{26}H_{25}NO_2PPdS]^+$ = 552.0373 $[M\text{-}DMSO+H]^+$; found *m/z* = 552.0373 $[M\text{-}DMSO+H]^+$.

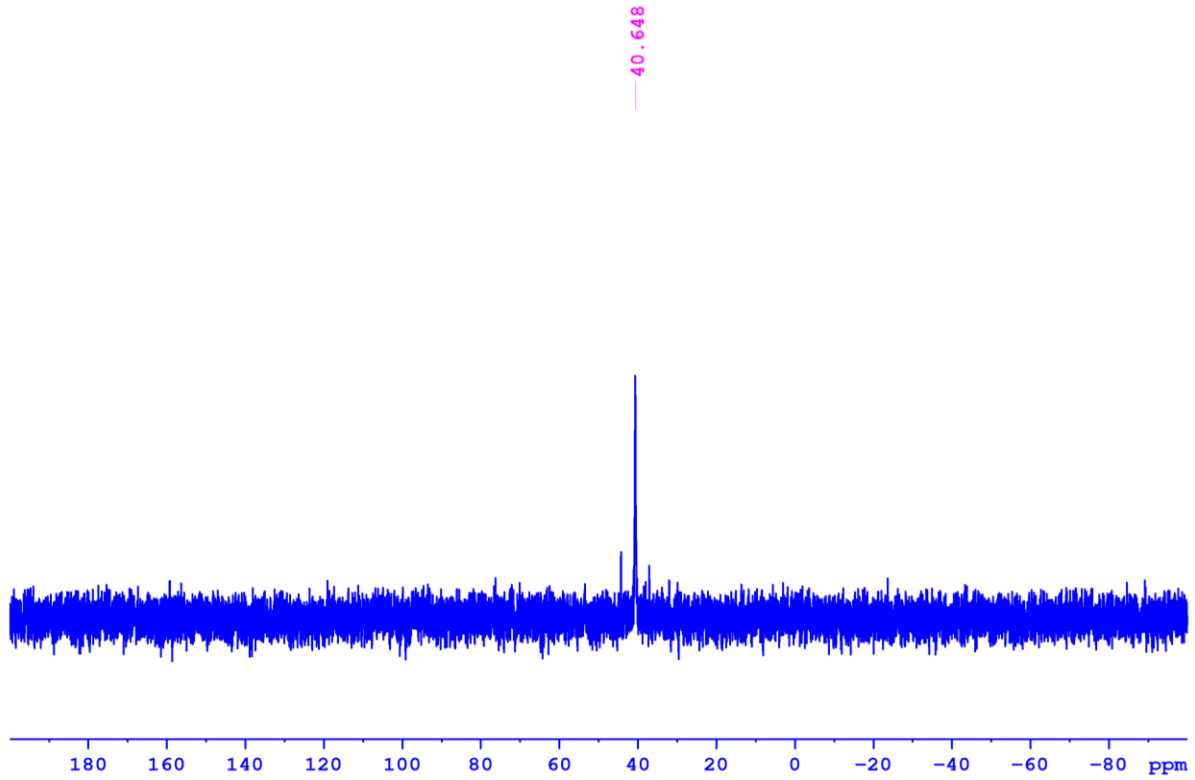



**Figure S66:** $^{31}P$ NMR spectrum of complex **C6** in $CDCl_3$.

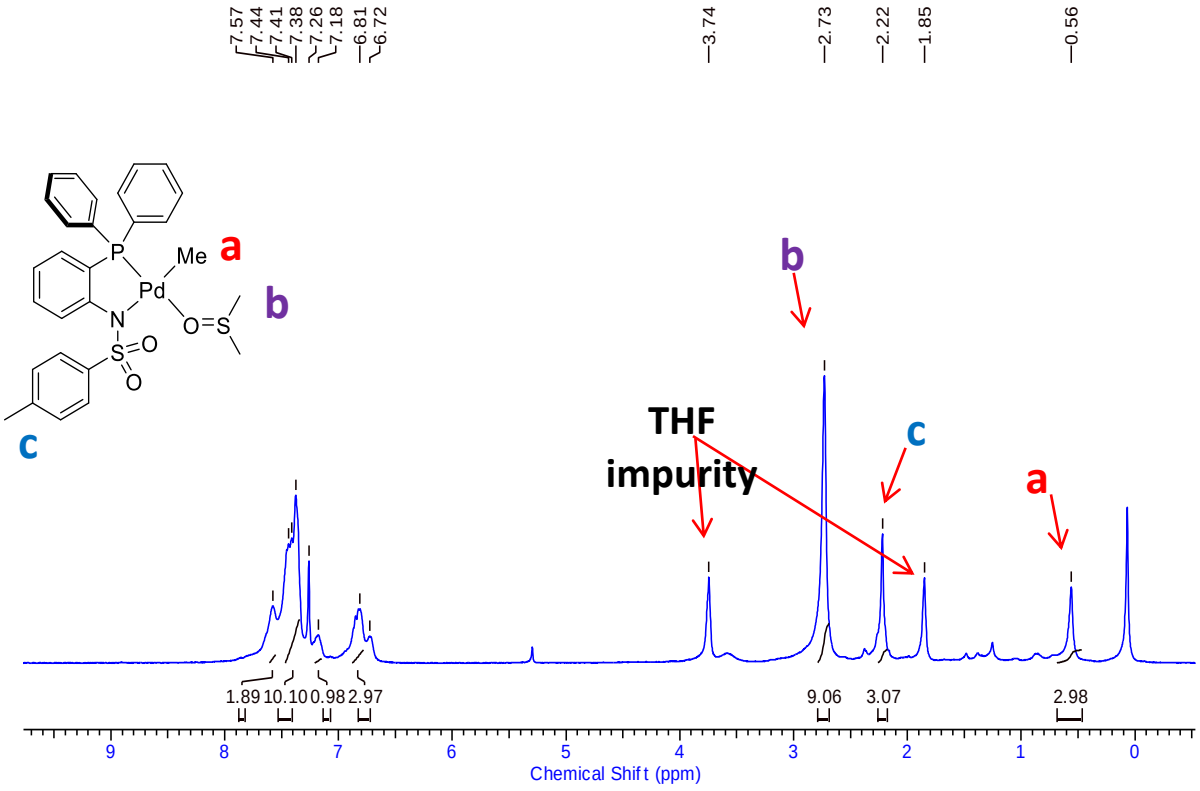



**Figure S67:** $^{1}H$ NMR spectrum of complex **C6** in $CDCl_3$.

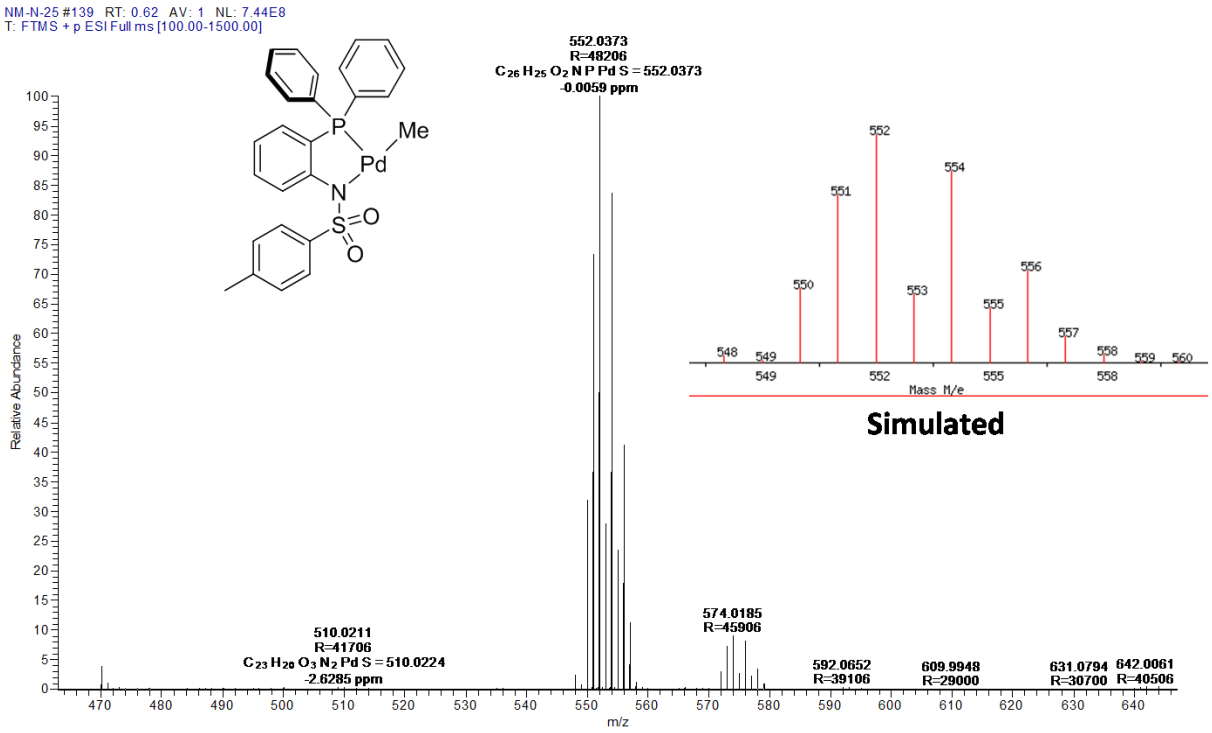
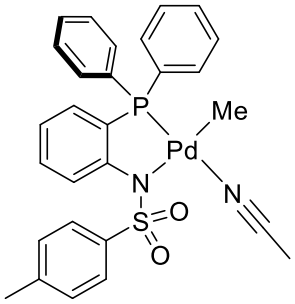



**Figure S68:** ESI-MS spectrum of complex **C6** in $CDCl_3$.

## 3.7. Palladium complex C7:




Ligand **L1B** (0.100 gm, 0.23 mmol) was treated with sodium hydride (0.005 gm, 0.23 mmol) in THF (5 mL) for 24 hours at room temperature. After evaporation of THF, the sodium salt of ligand **L1B** was suspended in acetonitrile (6 mL) and [(COD)PdMeCl] (0.061 gm, 0.23 mmol) was added. The reaction mixture was stirred at room temperature for 1 hour. Resulting turbid solution was passed through the bed of celite under argon. Volatiles were evaporated to obtain off white solid in 84 % isolated yield.

**$^{31}$P NMR** (400 MHz in $CDCl_3$): δ = 41.06. **$^{1}$H NMR** (400 MHz in $CDCl_3$): δ = 7.63 (s, 2H, Ar-H), 7.41-7.46 (m, 8H, Ar-H), 7.37 (m, 4H), 7.16 (m, 1H, Ar-H), 6.85 (m, 2H, Ar-H), 6.70 (m, 1H, Ar-H), 2.23 (s, 3H, *p*-OMe), 2.09 (s, 3H, MeCN), 0.49 (s, 3H, Pd-Me). **ESI-MS:** Calculated *m/z* for$[C_{28}H_{28}N_2O_2PPdS]^+$= 593.0644 $[M+H]^+$; found *m/z* = 593.0679 $[M+H]^+$.

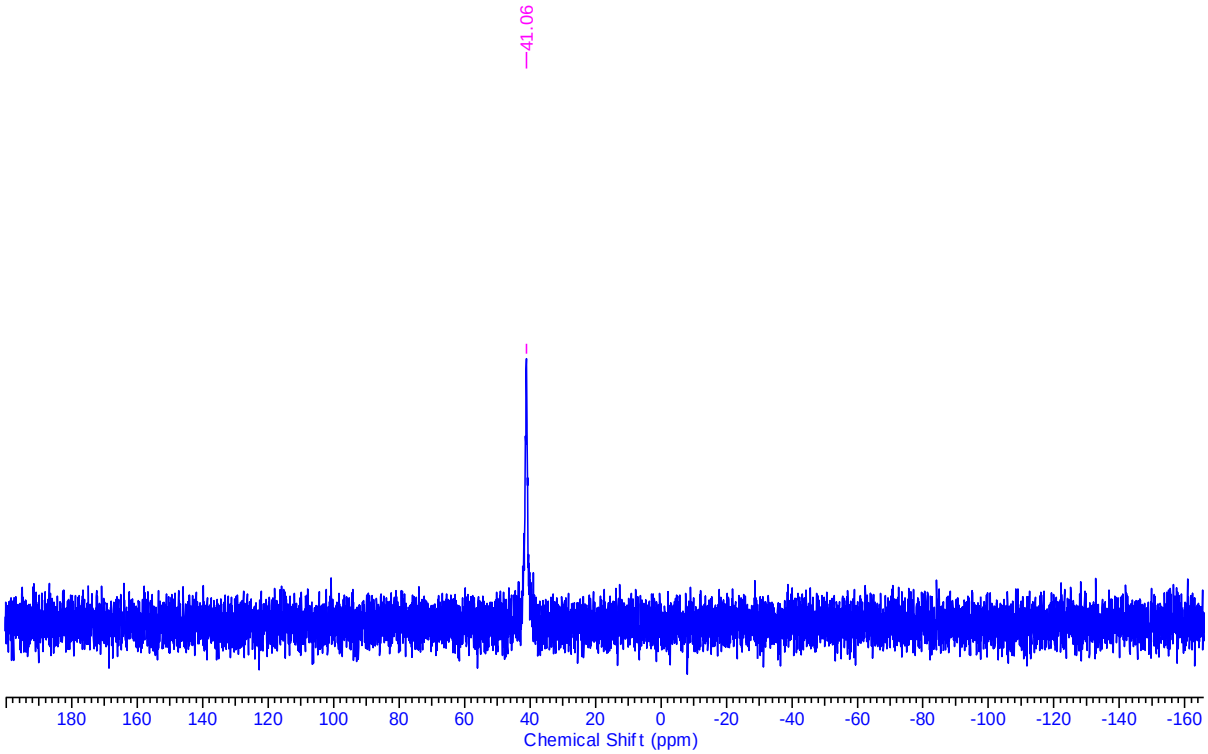



**Figure S69:** $^{31}$P NMR spectrum of complex **C7** in $CDCl_3$.

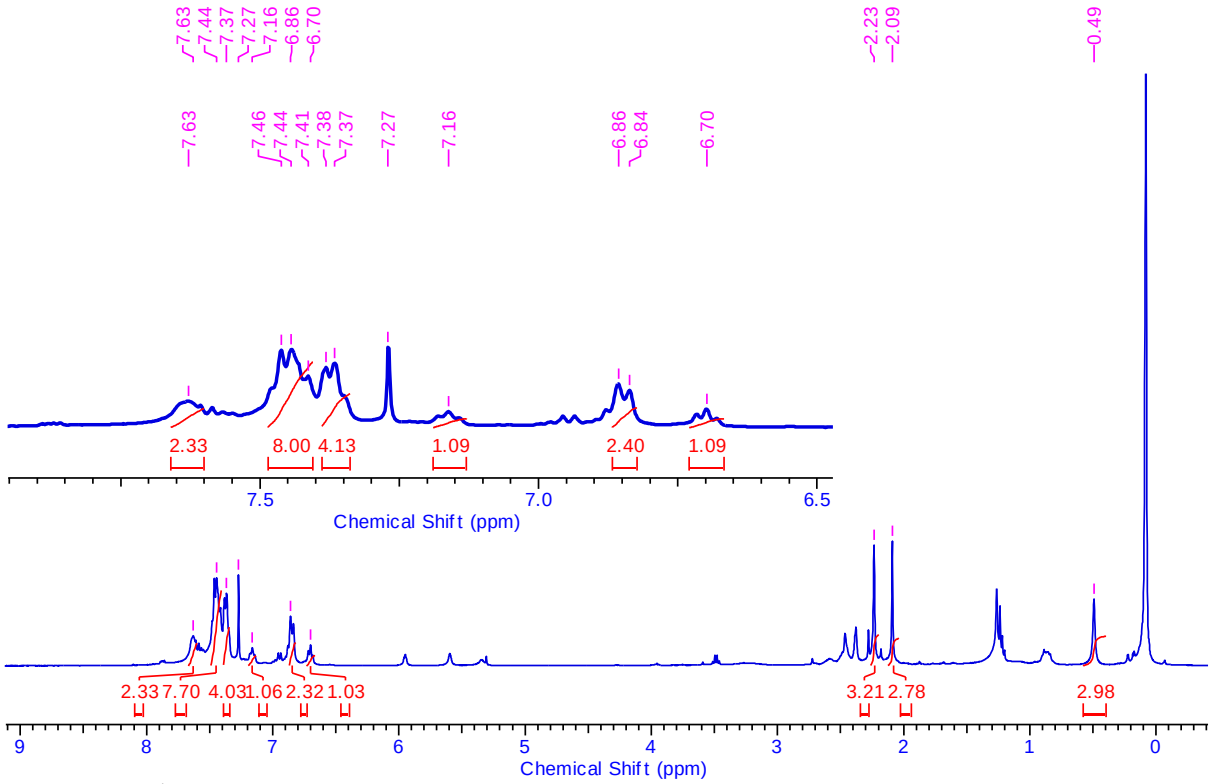



**Figure S70:** $^{1}$HNMR spectrum of complex **C7** in $CDCl_3$.

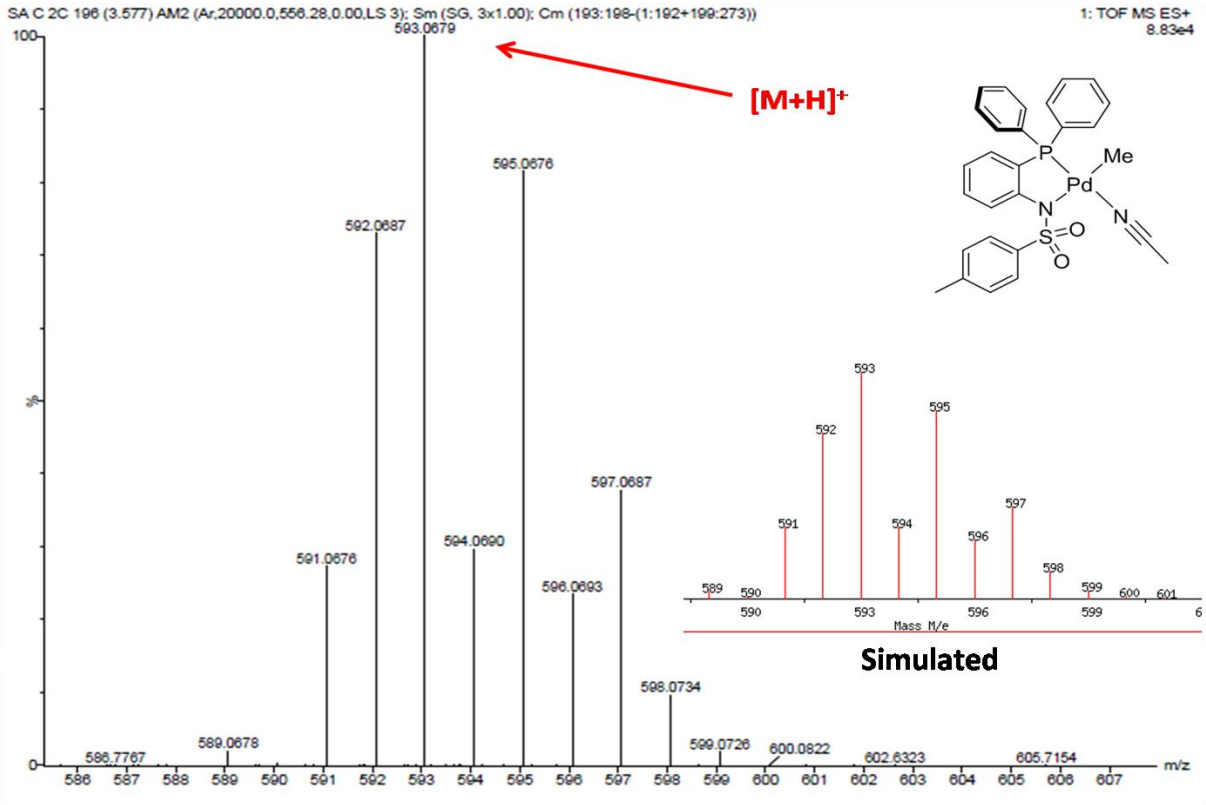



**Figure S71:** ESI-MS spectrum of complex **C7** in methanol.

## 4. Ethylene Oligomerization

Ethylene (4.5 grade) was supplied by Ms. Vadilal Chemicals Ltd. Pune, India. Ethylene oligomerization was carried out in a 250 mL stainless steel high-pressure Büchi (GlasUster cyclone 075) reactor equipped with a heating/cooling jacket and mechanical stirrer. Prior to the experiment, the reactor was fully dried by heating it in vacuum at 90 °C for 30 min, followed by cooling it to room temperature and filling it with argon. After cooling under argon, the reactor was flushed with ethylene (3 times, at the desired pressure) and was charged with appropriate quantity of toluene under positive ethylene pressure. The reactor was then pressurized to the desired pressure and saturated with ethylene for 30 min at the desired reaction temperature. After cooling to room temperature, the solution of catalysts (63 μmol in 10 mL DCM) was introduced into the reactor at room temperature. The reactor was finally pressurized to the desired ethylene pressure with stirring. The oligomerization was generally carried out for 1 h, the excess ethylene was slowly vented off, and the reactor was allowed to cool down to room temperature. Solvent was evaporated under reduced pressure at 45°C on rotavap. The resultant semi-solid/oil gray color material was weighed and characterized by various methods. It appears that ligand is decomposing and palladium

blacking is precipitating. Yield of the oligomers is calculated after subtracting the initial weight of the catalyst. Important polymerization experiments using catalysts **C1-C7** are summarized in Table 1.

**Table S6. Molecular weight of ethylene oligomers by GPC and $^{1}$H NMR spectroscopy.**

| Entry (Entry from Table 1) | Cat. | Temp. (°C) | Press. (bar) | Yield (mg) | TOF (mol of PE/mol of Pd/h) | Mn | |
|---|---|---|---|---|---|---|---|
| | | | | | | GPC | NMR |
| 1 (3) | C1 | 90 | 20 | 19 | 11 | 300 | |
| 2 (10) | C4 | 90 | 10 | 67 | 37 | 1100 | ~1100 |
| 3 (13) | C5 | 90 | 10 | 101 | 57 | 300 | - |
| 4 (15) | C5 | 100 | 20 | 104 | 58 | 1000 | ~800 |
| 5 (17) | C5 | 100 | 40 | 141 | 80 | 1100 | - |
| 6 (18) | C5 | 110 | 10 | 103 | 58 | 1000 | |
| 7 (22) | C5 | 120 | 40 | 97 | 55 | 1000 | ~1900 |
| 8 (26) | C6 | 90 | 10 | 43 | 24 | 300 | |

## 5. Characterization of ethylene oligomers:

$M_n$ by $^{1}$H NMR: The calculation of number average molecular weight by $^{1}$H NMR is well established in literature and we adopted the same method. The general formula used for $M_n$ calculation in reference method is a under[7]:

$$\frac{\text{peak area of repeating units and glycerol linkage}}{\text{\# of protons in repeating units and glycerol linkage}} = \frac{\text{peak area of end groups}}{\text{\# of protons in end groups}}$$

$$\frac{9.65}{12n+5} = \frac{1.00}{9},\ n = 6.82 \approx 7 \text{ repeating monomer units}$$

$$M_n = FW_{\text{glycerol linkage}} + FW_{\text{end groups}} + FW_{\text{repeating units}} = 41 + 177 + (44 \times 7 \times 3) = 1142$$

Thus, the $M_n$ for Table S6, entry 4 (see figure S72) is determined as under:

Degree of Polymerization (DP) = (Integral of the repeating unit / no. of protons of repeating unit) × (Peak area of end group / No. of protons in end group)

$M_n$ = DP × Molecular weight of repeating unit

**For figure S72:**

DP = 108.83/4 × 2/2

DP = 27.25 ~ 27 repeating units

$M_n$ = 27 × 28 = 756 ~800 Da

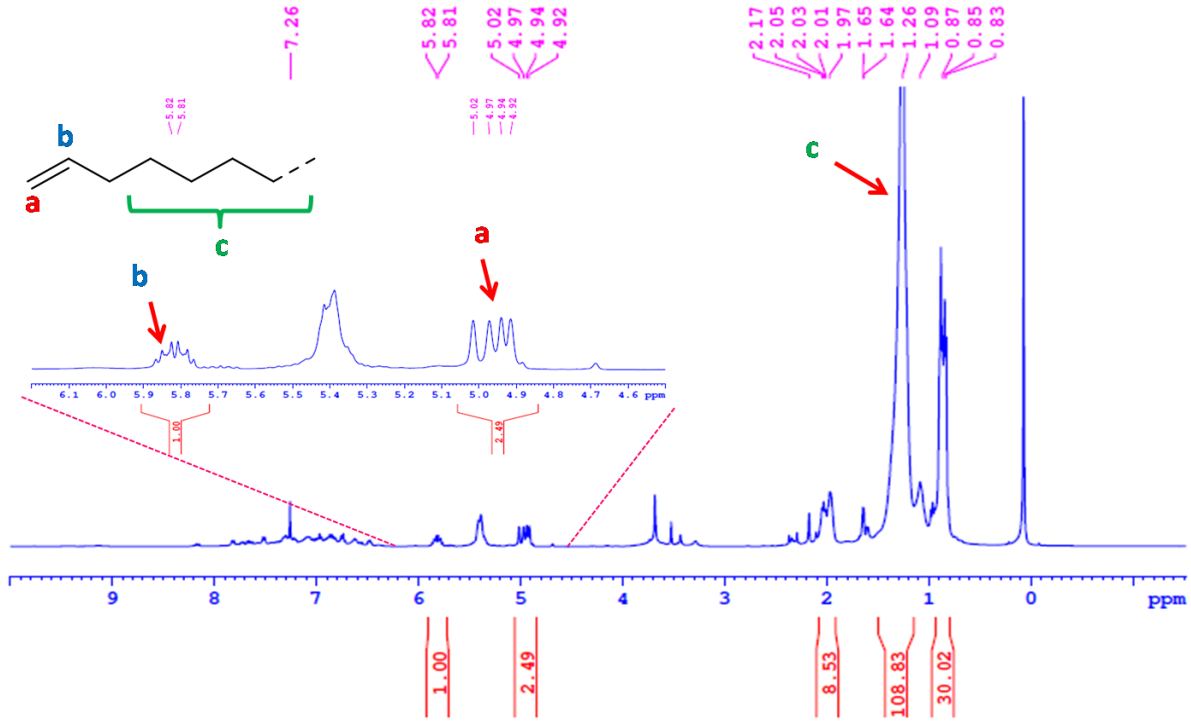



**Figure S72:** $^1$H NMR spectrum of ethylene oligomers obtained from entry 4 (table S6) in $CDCl_3$.

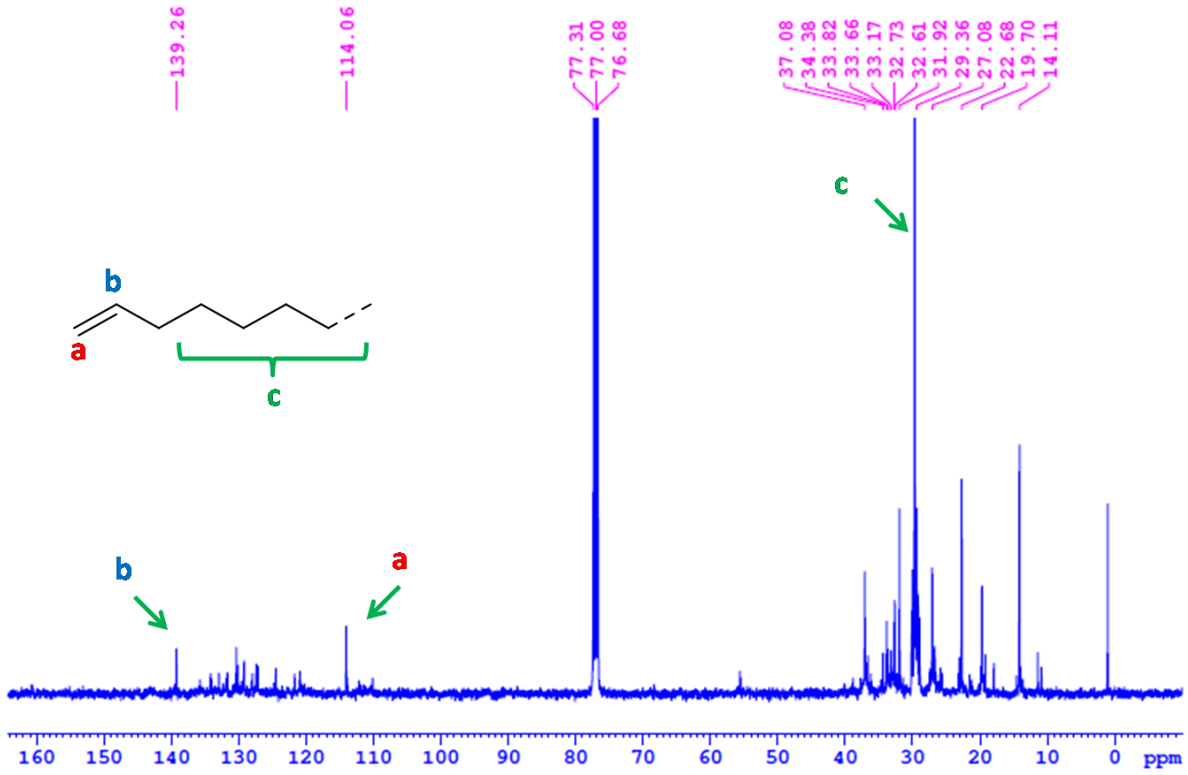



**Figure S73:** $^{13}C$ NMR spectrum of ethylene oligomers obtained from entry 4 (table S6) in $CDCl_3$.

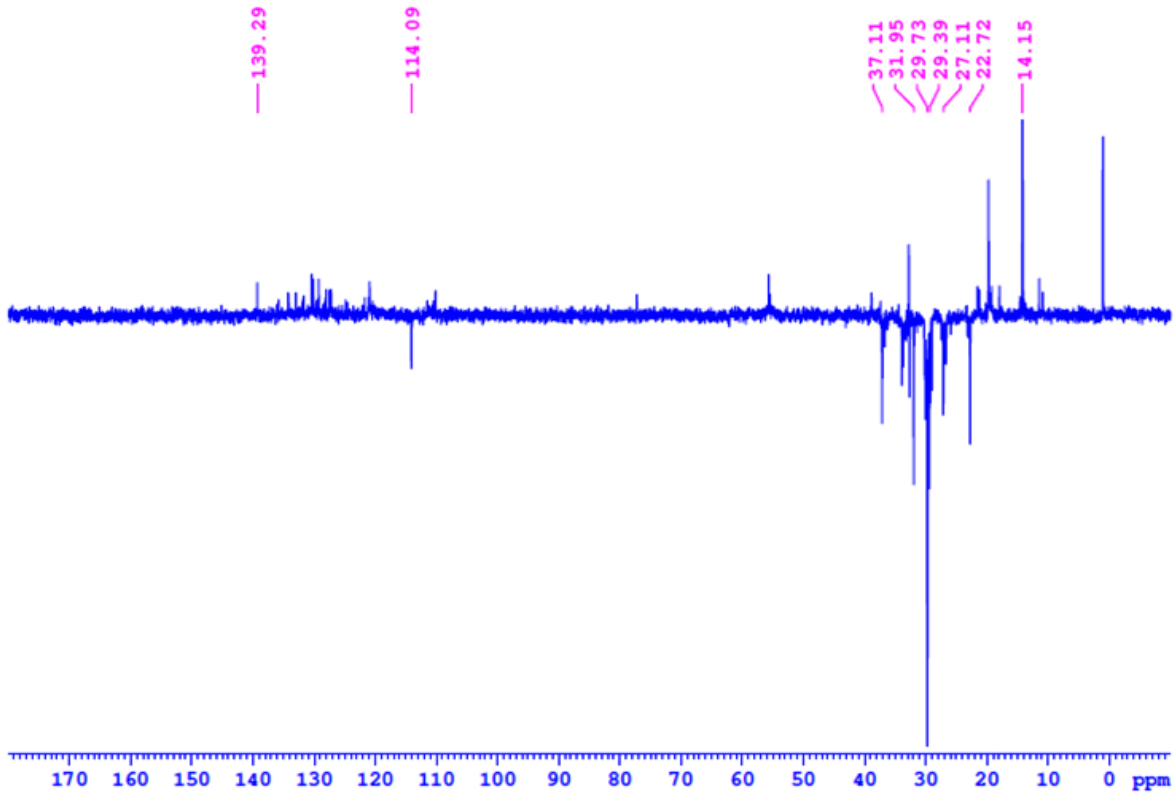



**Figure S74:** DEPT-NMR spectrum of ethylene oligomers obtained from entry 4 (table S6) in $CDCl_3$.

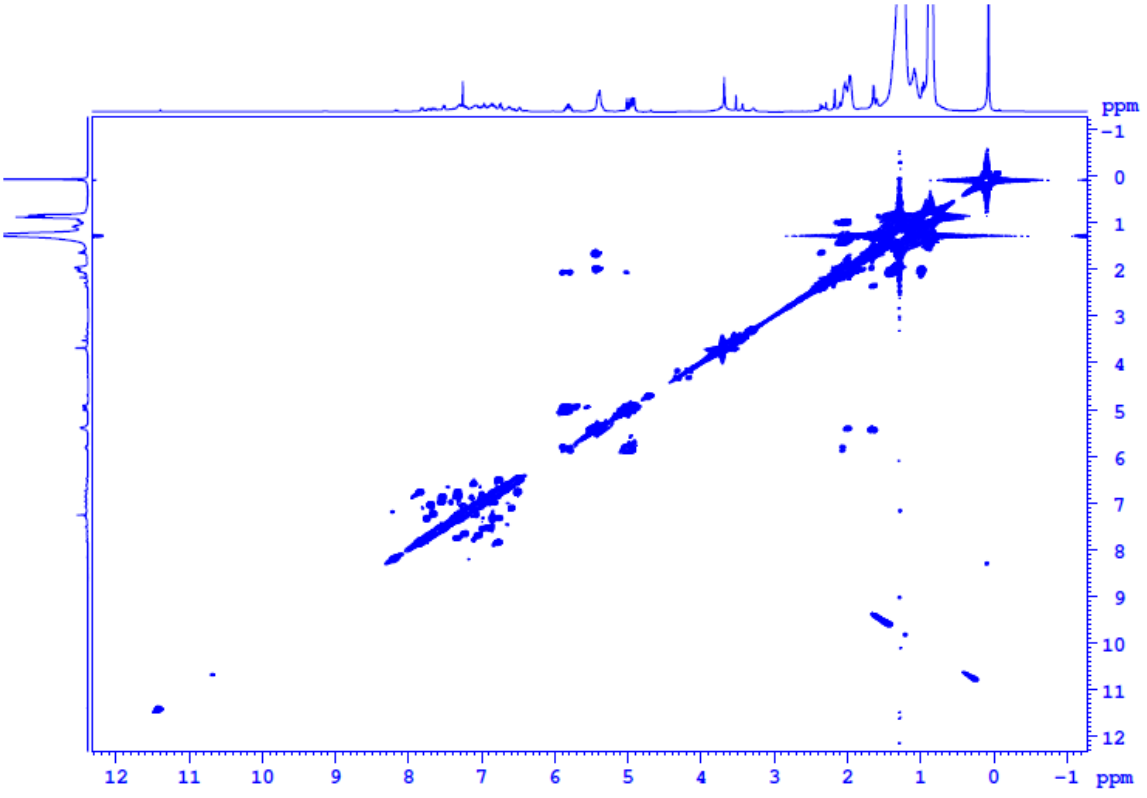



**Figure S75:** COSY-NMR spectrum of ethylene oligomers obtained from entry 4 (table S6) in $CDCl_3$.

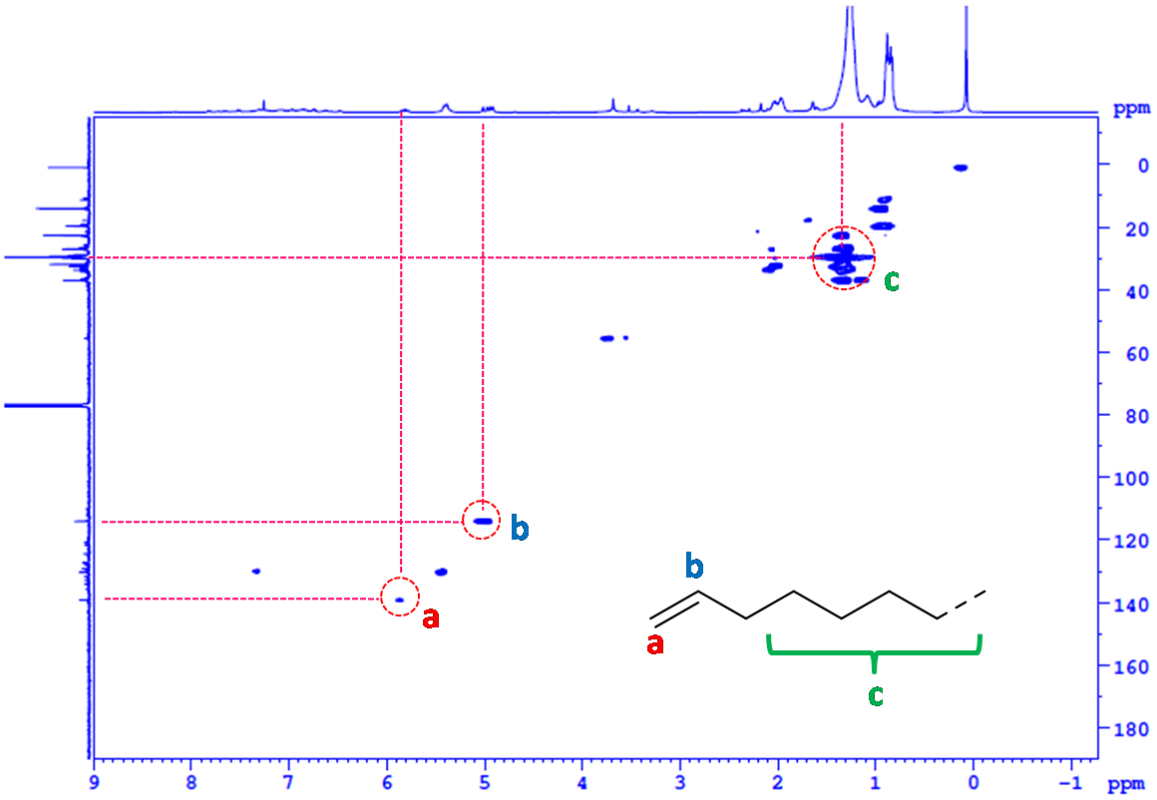



**Figure S76:** HSQC-NMR spectrum of ethylene oligomers obtained from entry 4 (table S6) in $CDCl_3$.

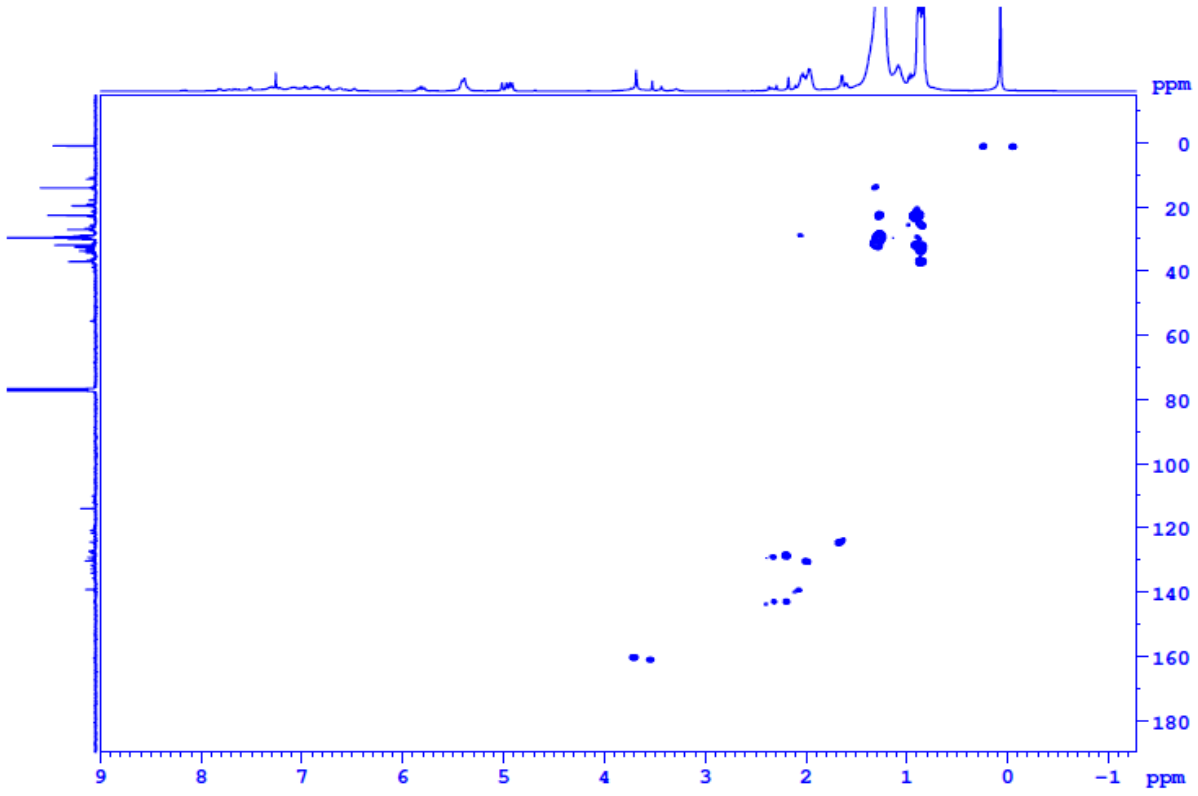



**Figure S77:** HMBC-NMR spectrum of ethylene oligomers obtained from entry 4 (table S6) in $CDCl_3$.

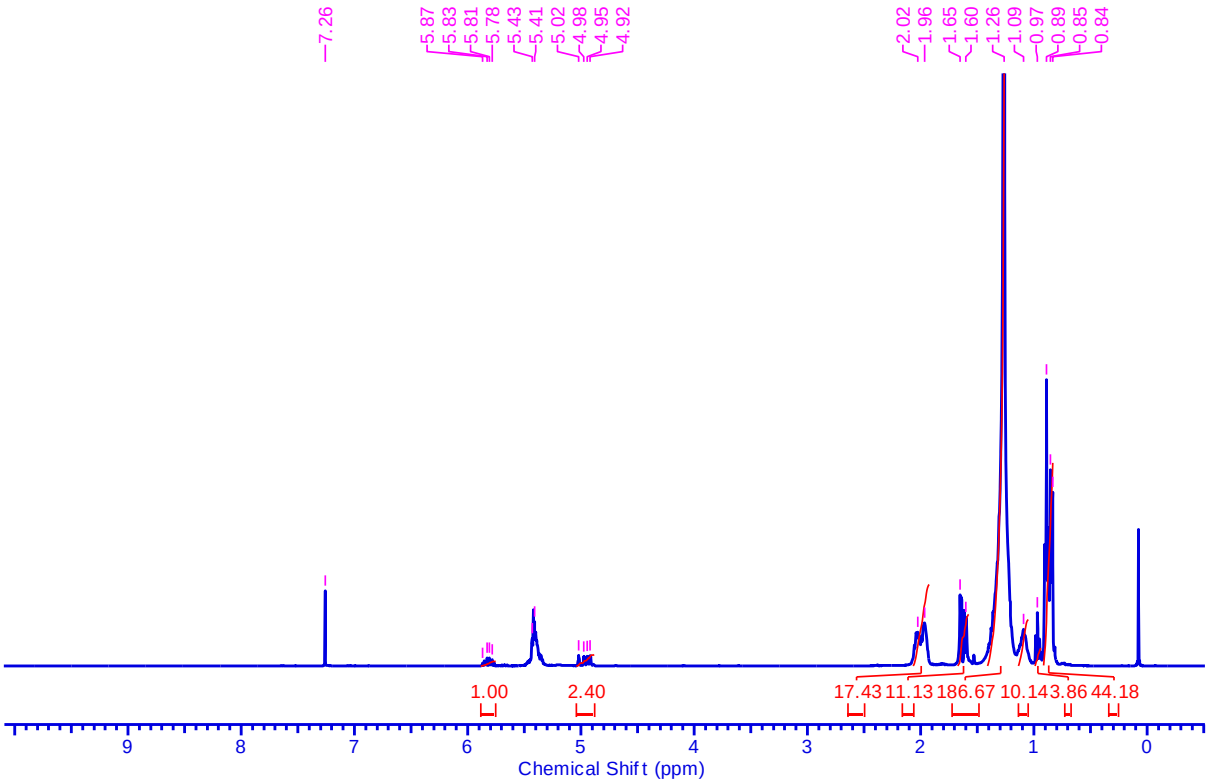
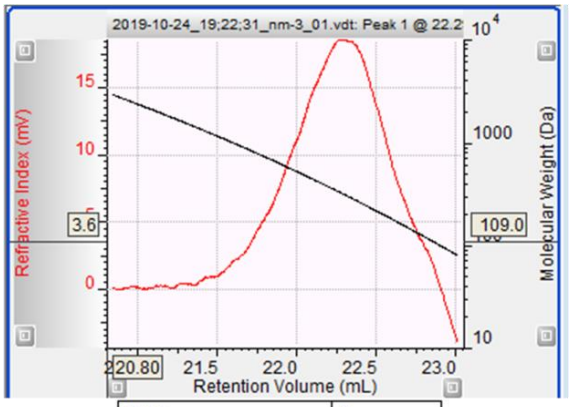


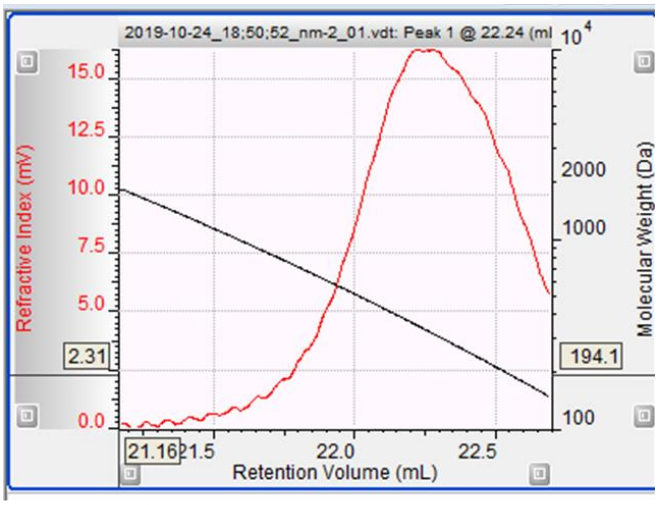

**Figure S78:** $^1H$ NMR spectrum of oligomers obtained from entry 22 (table 1) in $CDCl_3$.

## GPC data:



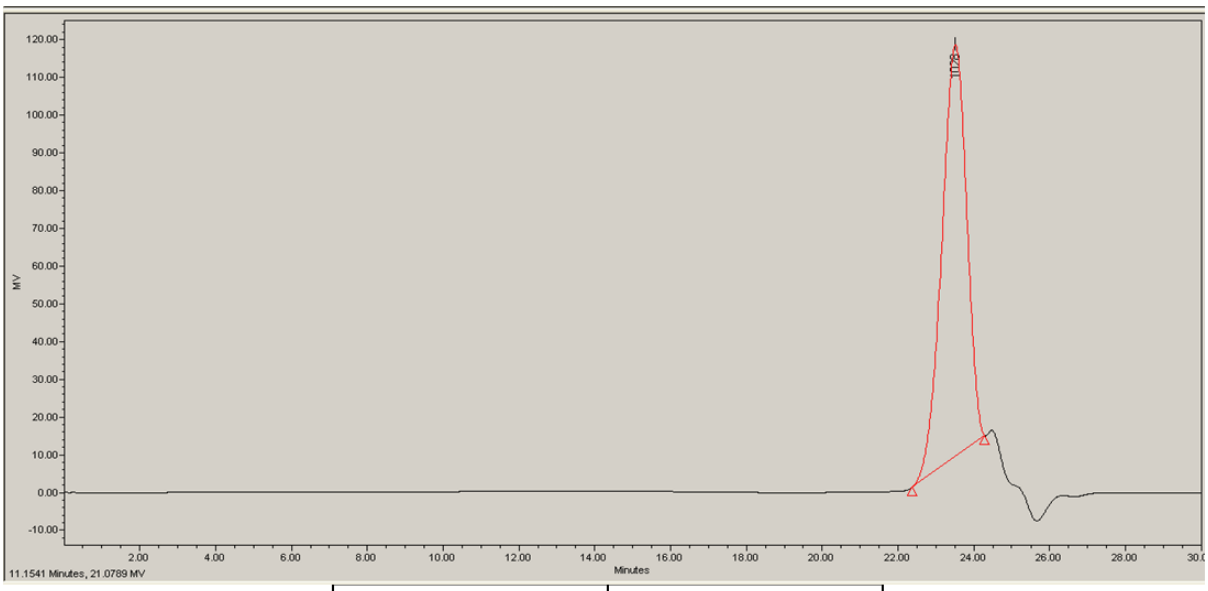

| Peak | 1 |
|---|---|
| Ret Vol (mL) | 22.287 |
| Mn (Da) | 315 |
| Mw (Da) | 407 |
| Mz (Da) | 601 |
| Mp (Da) | 311 |
| Mw/Mn | 1.291 |
| % Above 0 | 100.0000 |
| % Below 0 | 0.0000 |
| Wt Fr (Peak) | 1.0000 |

**Figure S79:** GPC chromatogram of oligomers obtained from entry 1 (table S6) in THF.



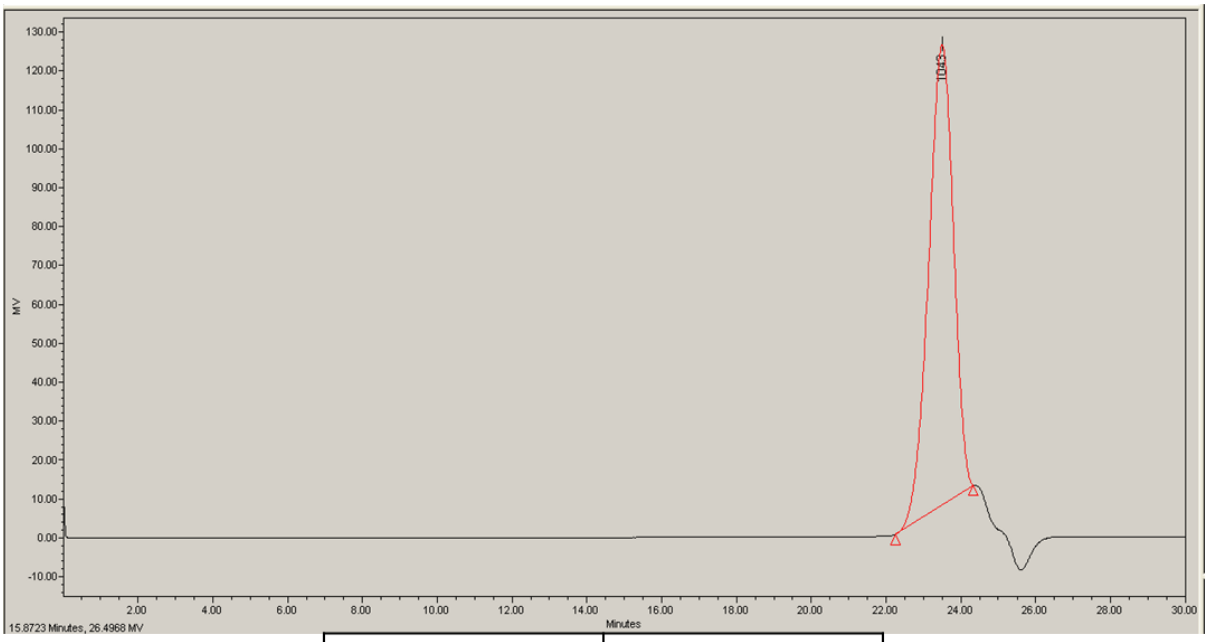

| Peak | 1 |
|---|---|
| Ret Vol (mL) | 22.243 |
| Mn (Da) | 305 |
| Mw (Da) | 374 |
| Mz (Da) | 494 |
| Mp (Da) | 335 |
| Mw/Mn | 1.228 |
| % Above 0 | 100.0000 |
| % Below 0 | 0.0000 |
| Wt Fr (Peak) | 1.0000 |
| RI Area (mVmL) | 10.38 |

**Figure S80:** GPC chromatogram of oligomers obtained from entry 3 (table S6) in THF.



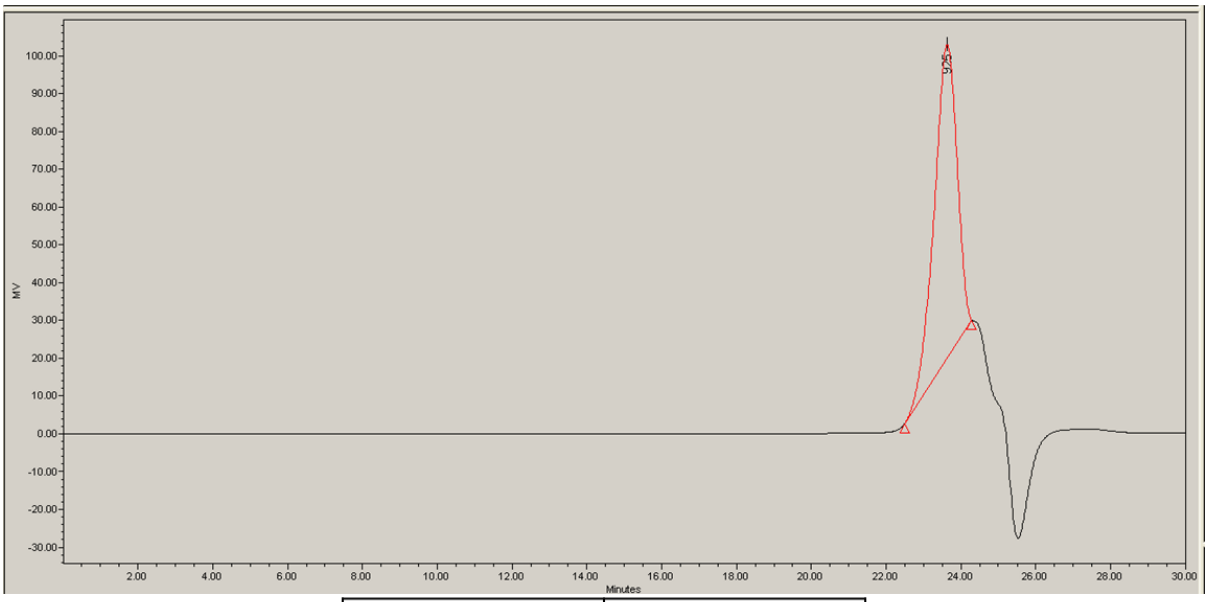

| | |
|---|---|
| **Peak** | **2** |
| **Ret Vol (mL)** | **23.517** |
| **Mn (Da)** | **1056** |
| **Mw (Da)** | **1127** |
| **Mz (Da)** | **1209** |
| **Mp (Da)** | **1028** |
| **Mw/Mn** | **1.066** |
| **% Above 0** | **100.00** |
| **% Below 0** | **0.00** |

**Figure S81:** GPC chromatogram of oligomers obtained from entry 2 (table S6) in THF.



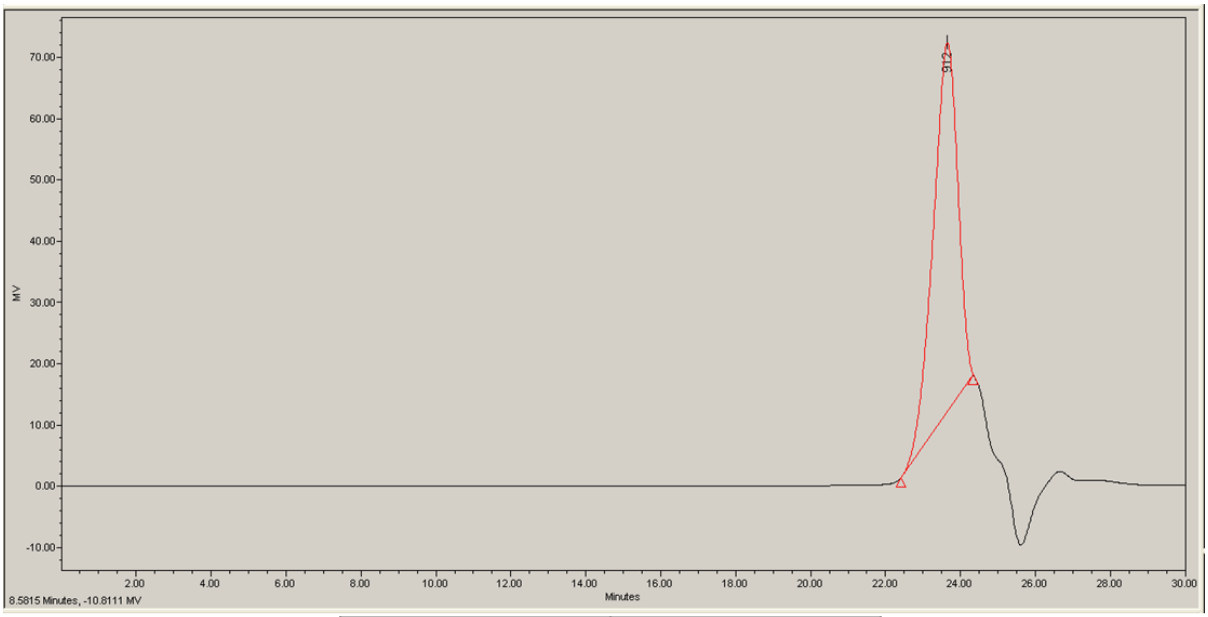

| Peak | 2 |
|---|---|
| Ret Vol (mL) | 23.502 |
| Mn (Da) | 1068 |
| Mw (Da) | 1142 |
| Mz (Da) | 1228 |
| Mp (Da) | 1043 |
| Mw/Mn | 1.069 |
| % Above 0 | 100.00 |
| % Below 0 | 0.00 |

**Figure S82:** GPC chromatogram of oligomers obtained from entry 5 (table S6) in THF.



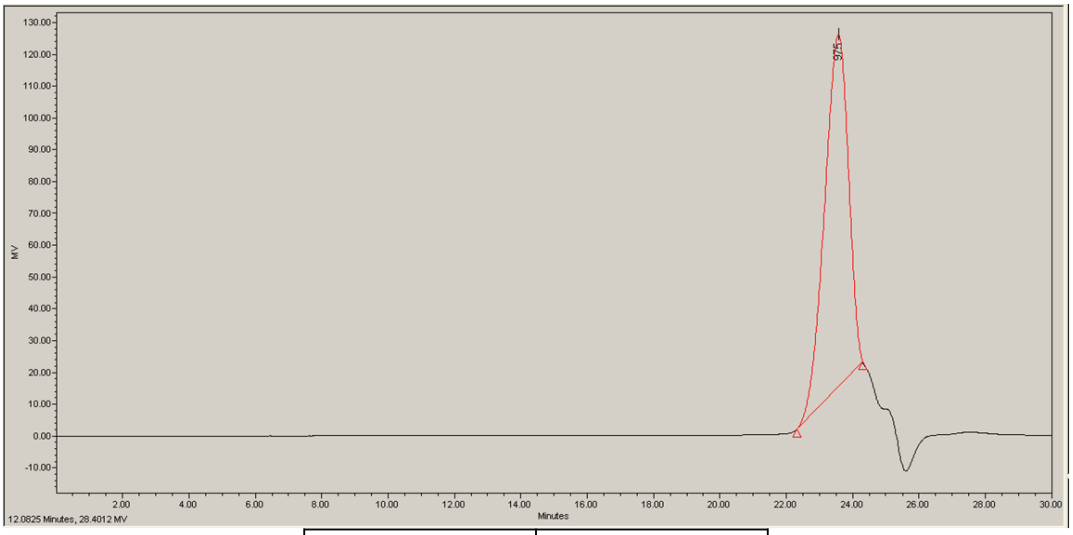

| Peak | 2 |
|---|---|
| Ret Vol (mL) | 23.635 |
| Mn (Da) | 982 |
| Mw (Da) | 1040 |
| Mz (Da) | 1108 |
| Mp (Da) | 925 |
| Mw/Mn | 1.058 |
| % Above 0 | 100.00 |
| % Below 0 | 0.00 |

**Figure S83:** GPC chromatogram of oligomers obtained from entry 4 (table S6) in THF.



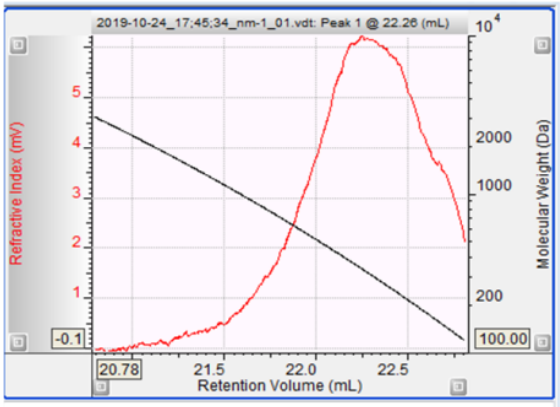

| Peak | 2 |
|---|---|
| Ret Vol (mL) | 23.651 |
| Mn (Da) | 984 |
| Mw (Da) | 1047 |
| Mz (Da) | 1122 |
| Mp (Da) | 912 |
| Mw/Mn | 1.063 |
| % Above 0 | 100.00 |
| % Below 0 | 0.00 |

**Figure S84:** GPC chromatogram of oligomers obtained from entry 6 (table S6) in THF.




| Peak | 1 |
|---|---|
| Ret Vol (mL) | 23.577 |
| Mn (Da) | 1044 |
| Mw (Da) | 1124 |
| Mz (Da) | 1219 |
| Mp (Da) | 975 |
| Mw/Mn | 1.076 |
| % Above 0 | 100.00 |
| % Below 0 | 0.00 |

**Figure S85:** GPC chromatogram of oligomers obtained from entry 7 (table S6) in THF.




| Peak | 1 |
|---|---|
| Ret Vol (mL) | 22.257 |
| Mn (Da) | 288 |
| Mw (Da) | 404 |
| Mz (Da) | 643 |
| Mp (Da) | 328 |
| Mw/Mn | 1.400 |
| % Above 0 | 100.0000 |
| % Below 0 | 0.0000 |
| Wt Fr (Peak) | 1.0000 |
| RI Area (mVmL) | 4.96 |
| UV Area (mVmL) | 0.00 |

**Figure S86:** GPC chromatogram of oligomers obtained from entry 8 (table S6) in THF.

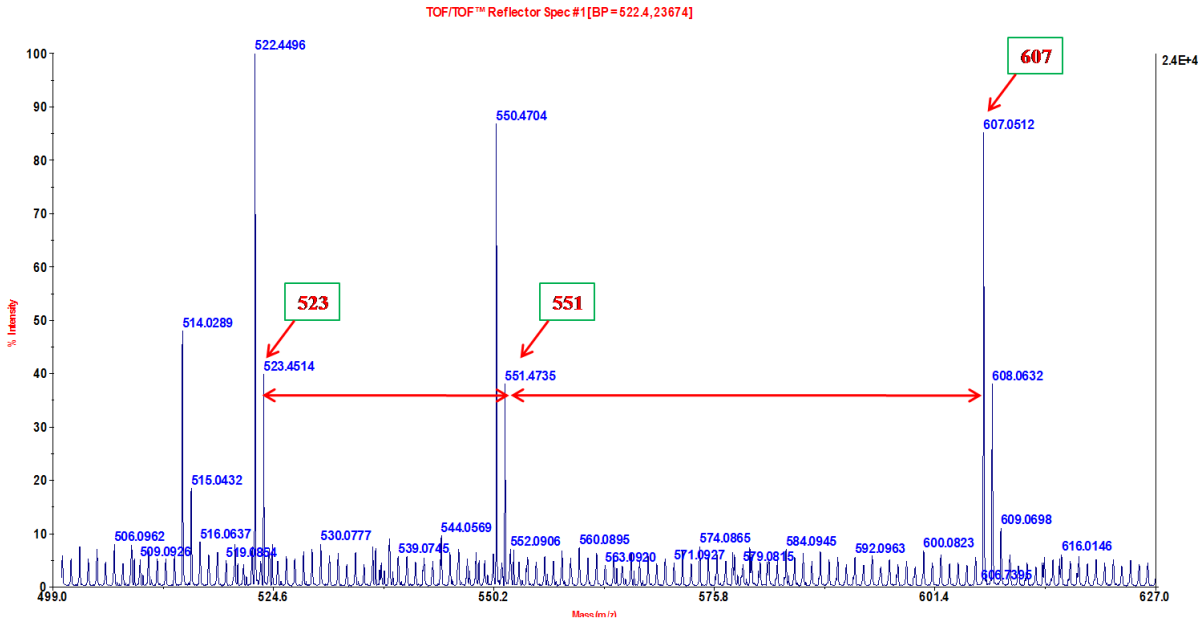



**Figure S87:** MALDI-ToF-MS analysis of oligoethylene from entry 17 (Table 1).

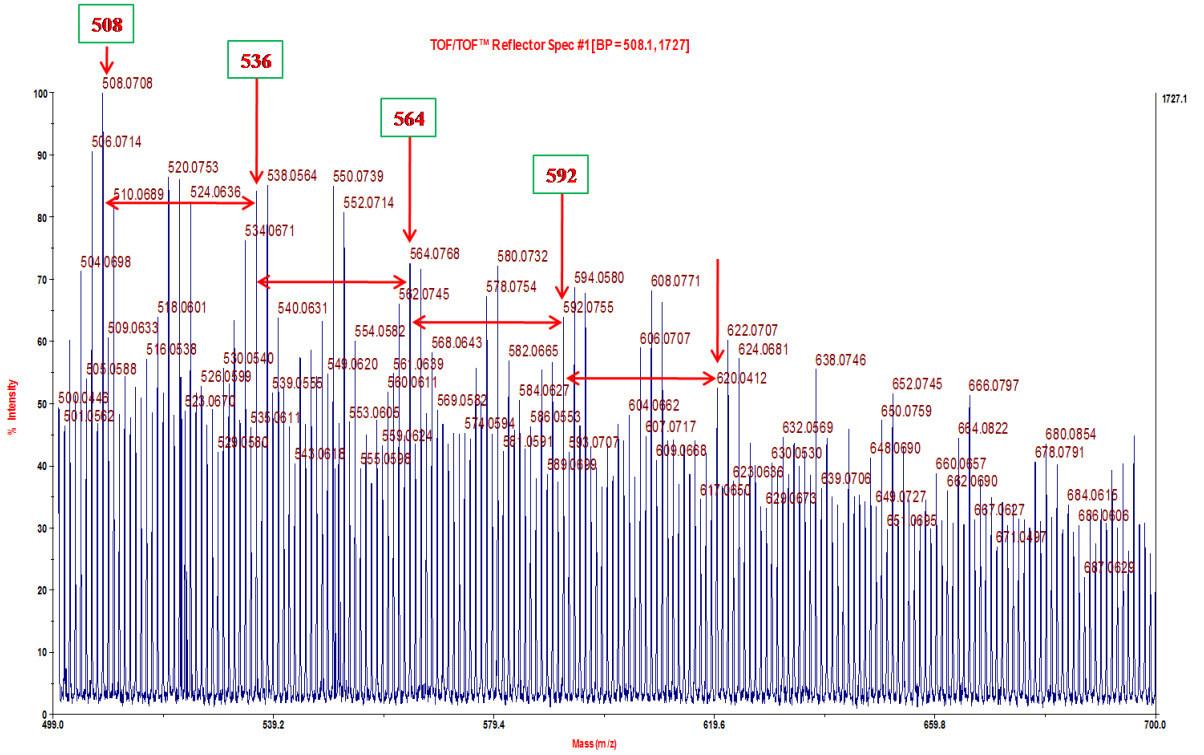



**Figure S88:** MALDI-ToF-MS analysis of oligoethylene from entry 13 table 1.

## 6. Catalyst stability study

Temperature dependent $^{31}P$ NMR study of catalyst **C1** was investigated. The NMR was recorded from room temperature to 80 °C temperature and it was found that there is no change in $^{31}P$ NMR chemical shift. This study suggest that the catalyst is stable at 80 °C.

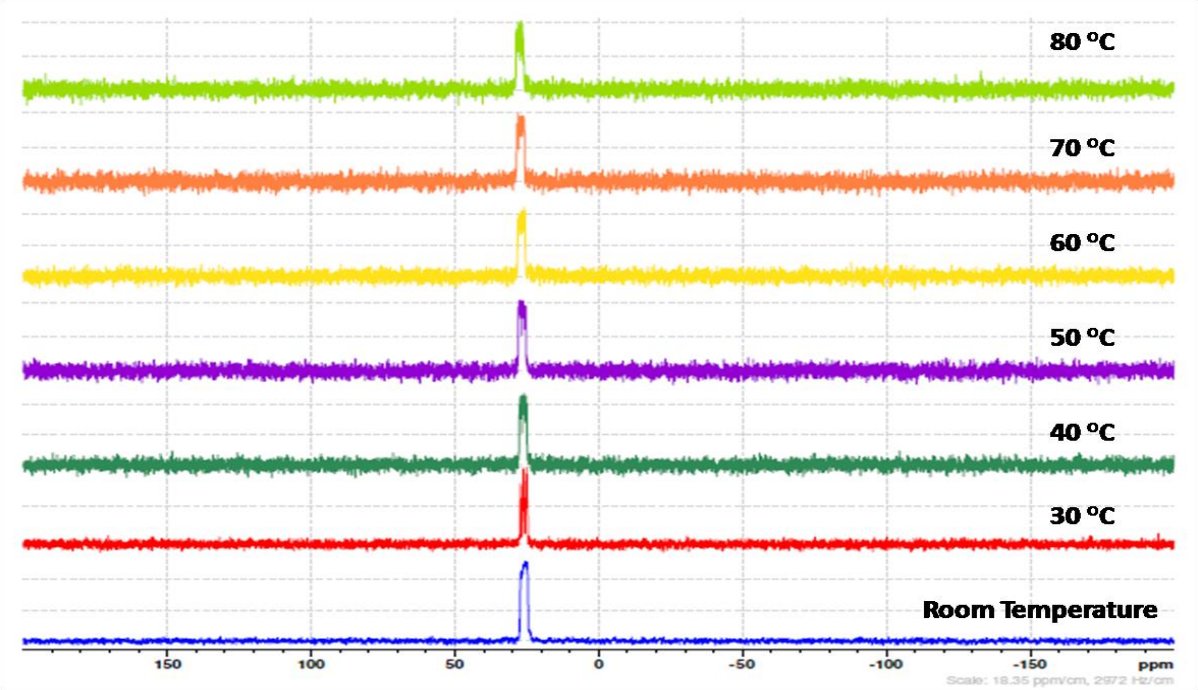



**Figure S89:** Temperature dependent catalyst study of complex C1 by $^{31}P$-NMR in $CDCl_3$.

## 7. Crystal data

**Table S7.** Comparison of bond distances of complexes **C1**, **C2** and **C3**.

| **Bonds** | **Distance (Å)** | | |
|---|---|---|---|
| | **C2** | **C1** | **C3** |
| Pd-C | 2.09 | 2.05 | 2.04 |
| Pd-P | 2.19 | 2.20 | 2.23 |
| Pd-$N^1$ | 2.12 | 2.13 | 2.12 |
| Pd-$N^2$ | 2.16 | 2.18 | 2.17 |

**Table S8.** Comparison of bond angles of complexes **C1**, **C2** and **C3**.

| **Bond angles** | **Angle (°)** | | |
|---|---|---|---|
| | **C2** | **C1** | **C3** |
| P-Pd-$N^2$ | 82.28 | 79.96 | 94.60 |
| P-Pd-C | 92.35 | 94.27 | 86.36 |
| C-Pd-$N^1$ | 90.70 | 86.71 | 88.93 |
| $N^1$-Pd-$N^2$ | 94.28 | 98.83 | 90.17 |

The crystal data for **L1A**, **L1B**, **C1**, **C2**, **C3** is summarized in Table S10.

**Table S9.**Crystal data table.

| | **L1A** | **L1B** | **C1** | **C2** | **C3** |
|---|---|---|---|---|---|
| Formula | $C_{27}H_{26}NO_4PS$ | $C_{25}H_{22}NO_2PS$ | $C_{33}H_{33}N_2O_4PPdS$ | $C_{31}H_{29}N_2O_2PPdS$ | $C_{33}H_{33}N_2O_4PPdS$ |
| $M_r$ | 491.52 | 431.46 | 691.04 | 630.99 | 691.04 |
| Crystal Size, mm | 0.20×0.17×0.03 | 0.19×0.11×0.07 | 0.19×0.03×0.02 | 0.24×0.19×0.03 | 0.20×0.17×0.03 |
| Temp. (K) | 100(2) | 100(2) | 100(2) | 100(2) | 100(2) |
| Crystal Syst. | Triclinic | Triclinic | monoclinic | Triclinic | Triclinic |
| Space Group | *P*-1 | *P*-1 | $P2_1/c$ | *P*-1 | *P*-1 |
| *a*/Å | 9.5013(4) | 10.0641(6) | 12.3236(13) | 9.466(7) | 9.959(2) |
| *b*/Å | 10.9649(4) | 10.8548(6) | 18.867(2) | 13.978(11) | 11.496(3) |
| *c*/Å | 13.6934(5) | 11.1095(6) | 13.3975(15) | 22.863(18) | 13.574(3) |
| $\alpha/^0$ | 73.562(2) | 76.414(2) | 90 | 74.14(2) | 91.745(8) |
| $\beta/^0$ | 70.075(2) | 81.176(2) | 105.039(4) | 87.92(2) | 100.761(8) |
| $\gamma/^0$ | 71.803(2) | 65.105(2) | 90 | 85.66(2) | 95.062(9) |
| $V$/Å$^3$ | 1248.98(9) | 1068.02(11) | 3008.4(6) | 2901(4) | 1519.0(6) |
| Z | 2 | 2 | 4 | 4 | 2 |
| $D_{calc}$/g cm$^{-3}$ | 1.307 | 1.342 | 1.526 | 1.445 | 1.511 |
| $\mu$/mm$^{-1}$ | 0.227 | 0.249 | 0.781 | 0.797 | 0.773 |
| *F(000)* | 516 | 452 | 1416 | 1288 | 708 |
| *Ab. Correct.* | multi-scan | multi-scan | multi-scan | multi-scan | multi-scan |
| $T_{min}$/ $T_{max}$ | 0.956/0.993 | 0.954/0.983 | 0.866/0.985 | 0.832/0.976 | 0.861/0.977 |
| $2\theta_{max}$ | 61.6 | 56 | 56 | 50.39 | 56 |
| Total reflections | 19104 | 71397 | 160280 | 30943 | 50137 |
| Unique reflections | 7686 | 5123 | 7256 | 10372 | 7286 |
| Observed reflections | 6027 | 4842 | 6681 | 7190 | 6609 |
| *h*, *k*, *l* (min, max) | (-12, 13), (-14, 15), | (-13, 13), (-14, 14), | (-16, 16), (-24, 24), | (-11, 11), (-16, 16), | (-13, 13), (-15, 15), |

| | (-19, 19) | (-14, 14) | (-17, 17) | (-27, 27) | (-17, 17) |
|---|---|---|---|---|---|
| $R_{int}$ | 0.0211 | 0.0305 | 0.0441 | 0.0727 | 0.0510 |
| $R_{sig}$ | 0.0271 | 0.0116 | 0.0113 | 0.0943 | 0.0302 |
| No. of parameters | 283 | 276 | 383 | 689 | 383 |
| No. of restraints | 0 | 0 | 0 | 0 | |
| *R1* [$I > 2\sigma(I)$] | 0.0473 | 0.0348 | 0.0237 | 0.0657 | 0.0273 |
| *wR2*[$I > 2\sigma(I)$] | 0.1235 | 0.0852 | 0.0568 | 0.1566 | 0.0689 |
| *R1* [all data] | 0.0625 | 0.0367 | 0.0274 | 0.0959 | 0.0318 |
| *wR2* [all data] | 0.1342 | 0.0865 | 0.0605 | 0.1679 | 0.0720 |
| goodness-of-fit | 1.030 | 1.052 | 1.075 | 1.137 | 1.062 |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$($eÅ^{-3}$) | +0.558, -0.557 | +1.176, -0.330 | +1.189, -1.012 | +1.138, -1.120 | +1.065, -0.631 |
| CCDC No. | 1977111 | 1977110 | 1977114 | 1977112 | 1977113 |

## 8. References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