Phenoxy-Linked Mesoionic Triazol-5-ylidenes as Platforms for Multinuclear Transition Metal Complexes

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Supporting information

Contents:

Experimental section

General methods

Commercially available reagents and solvents were used as received. Triazoles **I**, **II**, **IIA,** and **III**, were synthesized as reported in the literature.[1] All manipulations related to the synthesis of triazolium salts [**L1-H]**, [**L2-H_2],** [**L2A-H_2]**, and [**L3-H_3]** were performed under air. Synthesis of all metal complexes was performed under an atmosphere of dry nitrogen using standard Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen. Melting points were determined on a Fisher-Johns apparatus and are uncorrected. IR spectra were recorded on a Bruker Alpha FT-IR/ATR spectrometer. NMR and temperature dependent ^{1}H spectra (VT-NMR) were obtained with a Bruker Ascend (400 MHz) spectrometer. Elemental analyses were obtained with a Thermo Finnegan CHNSO-1112 apparatus and a Perkin Elmer Series II CHNS/O 2400 instruments. All thermograms were performed in a SDTQ600 equipment 20°C/min from room temperature to 700°C under nitrogen flow of 5 mL/min using alumina pan. GC-MS analyses were performed in an Agilent GC model HP 5890 coupled with a mass detector model 5973. X-Ray diffraction analyses were collected in an Agilent Gemini Diffractometer using Mo Kα radiation (l = 0.71073 Å). Data were integrated, scaled, sorted, and averaged using the CrysAlisPro software package. The structures we solved using direct methods, using SHELX 97 and refined by full matrix least squares against F^2.[2] All non hydrogen atoms were refined anisotropically. The position of the hydrogen atoms were kept fixed with common isotropic display parameters. The crystallographic data and some details of the data collection and refinement are given in Table 1. In the crystal structure of [**L2-H_2]** two highly disordered acetonitrile molecules were treated with the program SQUEEZE.[3] Corrections of the X-ray data for **[L2-H_2]** by SQUEEZE (47 electron cell) were close to the required values (44 electron cell).

Catalytic trials

General procedure for the alpha-arylation of propiophenone (Table 1).
The catalyst (2 mol%, based on metal), and NaO^tBu (1.5 mmol) were charged in a 5 mL screw capped vial equipped with a magnetic bar. 3 mL of anhydrous THF were added and the mixture was stirred for 5 minutes followed by the addition of the aryl bromide (1.1 mmol) and the propiophenone (1.5 mmol). The reaction mixture was heated at 80^{o}C for 2 h and the conversion was monitored by GC by taking aliquots every 20 minutes. The reaction mixture was purified directly by column chromatography on silica gel using 5-15% ethylacetate/hexane as eluent.

1-phenyl-2-(phenyl)-1-propanone (Table 1, entry 3): The general procedure afforded the title compound in 94% (217 mg, white solid) isolated yield after column chromatography using a mixture of 5:95 ethyl acetate/hexane as eluent. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.93 (d, *J* = 7.2 Hz, 2H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 2H), 7.30-7.21 (m, 5H), 4.72 (q, *J* = 7.2 Hz, 1H), 1.58 (d, *J* = 6.8 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 200.3, 141.5, 136.6, 132.8, 129.0, 128.8, 128.5, 127.7, 126.9, 47.9, 19.5.

1-phenyl-2-*p*-tolyl-1-propanone (Table 1, entry 6): The general procedure afforded the title compound in 94% (232 mg, white solid) isolated yield after column chromatography using a

mixture of 10:90 ethyl acetate/hexane as eluent. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.96 (d, *J* = 7.6 Hz, 2H), 7.47 (t, *J* = 8.2 Hz, 1H), 7.36 (t, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 4.71 (q, *J* = 6.8 Hz, 1H), 2.32 (s, 3H) 1.58 (d, *J* = 6.8 Hz, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 200.4, 138.4, 136.5, 136.5, 132.5, 129.7, 128.7, 128.4, 127.6, 47.5, 21.0, 19.5.

1-phenyl-2-*p*-cyanophenyl-1-propanone (Table 1, entry 9): The general procedure afforded the title compound in 95% (246 mg, white solid) isolated yield after column chromatography using a mixture of 10:90 ethyl acetate/hexane as eluent. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.95 (d, *J* = 7.2, 2H), 7.52 (t, *J* = 6.4 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.23-7.29 (m, 4H), 4.71 (q, *J* = 6.9 Hz, 1H), 1.55 (d, *J* = 6.9 Hz, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 200.4, 138.6, 135.9, 133.4, 132.7, 128.8, 128.7, 118.7, 110.9, 47.7, 19.4.

1-phenyl-2-*p*-methoxyphenyl-1-propanone (Table 1, entry 12): The general procedure afforded the title compound in 93% (246 mg, off white solid) isolated yield after column chromatography using a mixture of 15:85 ethyl acetate/hexane as eluent. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.98 (d, *J* = 7.2, 2H), 7.49 (t, *J* = 6.4 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.23 (d, *J* = 6.8 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 4.68 (q, *J* = 6.8 Hz, 1H), 3.75 (s, 3H), 1.55 (d, *J* = 6.8 Hz, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 200.5, 158.5, 136.6, 133.5, 132.7, 128.8, 128.9, 128.5, 128.4, 114.3, 55.2, 47.0, 19.5.

1-phenyl-2-*p*-nitrophenyl-1-propanone (Table 1, entry 15): The general procedure afforded the title compound in 88% (247 mg, white solid) isolated yield after column chromatography using a mixture of 10:90 ethyl acetate/hexane as eluent. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 7.2, 2H), 7.52 (t, *J* = 6.4 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.24-7.29 (m, 4H), 4.70 (q, *J* = 6.9 Hz, 1H), 1.55 (d, *J* = 6.9 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 199.9, 139.9, 136.3, 133.0, 132.8, 129.2, 129.1, 128.7, 128.6, 47.1, 19.4.

General procedure for the Suski-Miyarura coupling (Table 2).

Cesium carbonate (2 mmol) and boronic acid (1.3 mmol) were charged in a 10 mL screw capped vial equipped with a magnetic bar. The catalyst (3 mol%, based on metal) and 5 mL of anhydrous toluene were added and the mixture was stirred for 15 minutes. The arylbromide (1 mmol) was added in one portion, and the reaction mixture was heated at 120^{o}C for 2 hours and monitored by GC. Water was added to the reaction mixture, the organic layer was extracted with ethyl acetate, dried with magnesium sulfate, and the solvent was evaporated under vacuum. When necessary the product was purified by column chromatography on silica gel using 5-10% ethyl acetate/hexanes as eluent.

Biphenyl (Table 2, entry 4): The general procedure afforded the title compound in 91% (140 mg, off white solid) isolated yield after column chromatography using a mixture of 5:95 ethyl acetate/hexane as eluent. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.62-7.64 (dd, *J* = 7.8 Hz, 4H), 7.46-7.49 (t, *J* = 7.8 Hz, 4H), 7.37-7.39 (t, *J* = 7.8 Hz, 2H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 141.4, 128.9, 127.4, 127.3.

4-Methoxybiphenyl (Table 2, entry 8): The general procedure afforded the title compound in 91% (168 mg, white solid) isolated yield after column chromatography using a mixture of 10:90 ethyl

acetate/hexane as eluent. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.55-7.28 (m, 7H, ArH), 6.96 (d, 2H, *J* = 9.1 Hz, ArH), 3.81 (s, 3H, CH_3); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ = 159.3, 140.9, 133.9, 128.8, 128.3, 126.8, 126.7, 114.3, 55.4.

4-Methylbiphenyl (Table 2, entry 12): The general procedure afforded the title compound in 95% (160 mg, off white solid) isolated yield after column chromatography using a mixture of 5:95 ethyl acetate/hexane as eluent. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.69-7.70 (d, *J* = 7.8 Hz, 2H), 7.60-7.62 (d, *J* = 8.4 Hz, 2H), 7.52-7.54 (t, *J* = 7.8 Hz, 2H), 7.42-7.44 (t, *J* = 7.8 Hz, 1H), 7.35-7.36 (d, *J* = 7.8 Hz, 2H), 2.50 (s, 3H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 141.3, 138.5, 137.1, 6 130.9, 129.6, 128.8, 127.2, 127.1, 21.2.

4,4'-Dimethylbiphenyl (Table 2, entry 16): The general procedure afforded the title compound in 86% (157 mg, white solid) isolated yield after column chromatography using a mixture of 5:95 ethyl acetate/hexane as eluent. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.47 (d, *J* = 8.2 Hz, 4H), 7.23 (d, *J* = 7.9 Hz, 4H), 2.38 (s, 6H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 138.3, 136.7, 129.4, 126.8, 21.1.

General procedure for methoxycyclization of enyne E1 (Scheme 6).

Enyne **E1** (120 mg, 0.50 mmol) was dissolved in a 5 mL mixture 1:1 of methanol:CH_2Cl_2 followed by the addition of the precatalyst **Ln·**$[AuCl]_n$ (5 mol %, based on metal) and $AgSbF_6$ (5 mol %). The resulting solution was stirred at room temperature for 24 h. The solvent was removed under vacuum and the crude material was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (9:1) as eluent to give product **C1** as yellow oil in good yields. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 5.01 (bs, 1H), 4.95 (bs, 1H), 3.72 (s, 3H), 3.71 (s, 3H), 2.93-2.74 (m. 3H), 2.51 (dd, *J* = 10, 4 Hz, 1H), 1.99 (dd, *J* = 16, 10 Hz, 1H), 1.15 (s, 3H), 1.10 (s, 3H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 172.1, 171.9, 148.2, 110.6, 72.8, 58.6, 52.7, 52.6, 49.1, 43.4, 36.0, 22.7, 22.2.

Catalytic poisoning tests

Methoxycyclization of enyne E1

Mercury poisoning tests. Enyne **E1** (120 mg, 0.50 mmol) was dissolved in a 5 mL mixture 1:1 of methanol:CH_2Cl_2 followed by the addition of the appropriate precatalyst **Ln·**$[AuCl]_n$ (5 mol %, based on metal) and $AgSbF_6$ (5 mol %). To the resulting solution an excess amount of Hg (2.5 mmol) was added at different reaction times (t = 4, 8, 12, 16 and 20 h) and stirred at room temperature for 24 h. Aliquots (~ 10 μL) were removed every 4 h and analyzed by gas chromatography.

DCT (dibenzo[a,e]cyclooctatriene) poisoning tests. Enyne **E1** (120 mg, 0.50 mmol) was dissolved in a 5 mL mixture 1:1 of methanol:CH_2Cl_2 followed by the addition of the appropriate precatalyst

Ln·$[AuCl]_n$ (5 mol %, based on metal) and $AgSbF_6$ (5 mol %). To the resulting solution a slight excess of DCT (0.65 mmol) was added at different reaction times (t = 4, 8, 12, 16 and 20 h) and stirred at room temperature for 24 h. Aliquots (~ 10 μL) were removed every 4 h and analyzed by gas chromatography.

Alpha arylation of propiophenone

Mercury poisoning tests. The catalyst (2 mol%, based on metal), and NaO^tBu (1.5 mmol) were charged in a 5 mL screw capped vial equipped with a magnetic bar. 3 mL of anhydrous THF were added and the mixture was stirred for 5 minutes followed by the addition of the aryl bromide (1.1 mmol) and the propiophenone (1.5 mmol). To the reaction mixture an excess amount of Hg (5.2 mmol) was added at different reaction times (t = 0, 30, 60, and 90 min). After addition of mercury, every reaction mixture was heated at 80°C for 2 h. Aliquots (~ 10 μL) were removed every 20 minutes and analyzed by gas chromatography.

DCT (dibenzo[a,e]cyclooctatriene) poisoning tests. The catalyst (2 mol%, based on metal), and NaO^tBu (1.5 mmol) were charged in a 5 mL screw capped vial equipped with a magnetic bar. 3 mL of anhydrous THF were added and the mixture was stirred for 5 minutes followed by the addition of the aryl bromide (1.1 mmol) and the propiophenone (1.5 mmol). To the reaction mixture a slight amount of DCT (1.6 mmol) was added at different reaction times (t = 0, 30, 60, and 90 min). After addition of DCT, every reaction mixture was heated at 80°C for 2 h. Aliquots (~ 10 μL) were removed every 20 minutes and analyzed by gas chromatography.

Suzuki-Miyarura

Mercury poisoning tests. To the reaction mixture of the appropriate catalyst (2 mol%, based on metal), cesium carbonate (2 mmol), boronic acid (1.3 mmol) and bromobenzene (1 mmol) in 5 mL of dry toluene was added an excess amount of Hg (5 mmol) at different reaction times (t = 0, 30, 60 and 90 min). After addition of elemental mercury, every reaction mixture was heated at 120°C for 2 h. Aliquots (~ 10 μL) were removed every 20 minutes and analyzed by gas chromatography.

DCT (dibenzo[a,e]cyclooctatriene) poisoning tests. To the reaction mixture of the appropriate catalyst (2 mol%, based on metal), cesium carbonate (2 mmol), boronic acid (1.3 mmol) and bromobenzene (1 mmol) in 5 mL of dry toluene was added a slight excess amount of DCT (1.5 mmol) at different reaction times (t = 0, 30, 60, and 90 min). After the addition of DTC every reaction mixture was heated at 120°C for 2 h. Aliquots (~ 10 μL) were removed every 20 minutes and analyzed by gas chromatography.

References:

1) (a) Mendoza-Espinosa, D.; Negrón-Silva, G.; Lomas-Romero, L.; Gutiérrez-Carrillo, A.; Soto-Castro, D. *Synthesis*, **2013**, *45*, 2431-2437. (b) Mendoza-Espinosa, D.; Negrón-Silva, G.; Lomas-Romero, L.; Gutiérrez-Carrillo, A.; Santillán, R. *Synthetic Commun.* **2014**, *44*, 807-817.

2) Sheldrick, G. M. *SHELXS-97, Program for Crystal Structure Solution and Refinement*; Institut Für Anorganishe Chemie, Göttingen, Germany, 1998.
3) Van der Sluis, P. V.; Speck, A. L. *Acta Crystallogr., Sect. A: Fundam. Crystallogr.,* **1990**, *46*, 194–201.

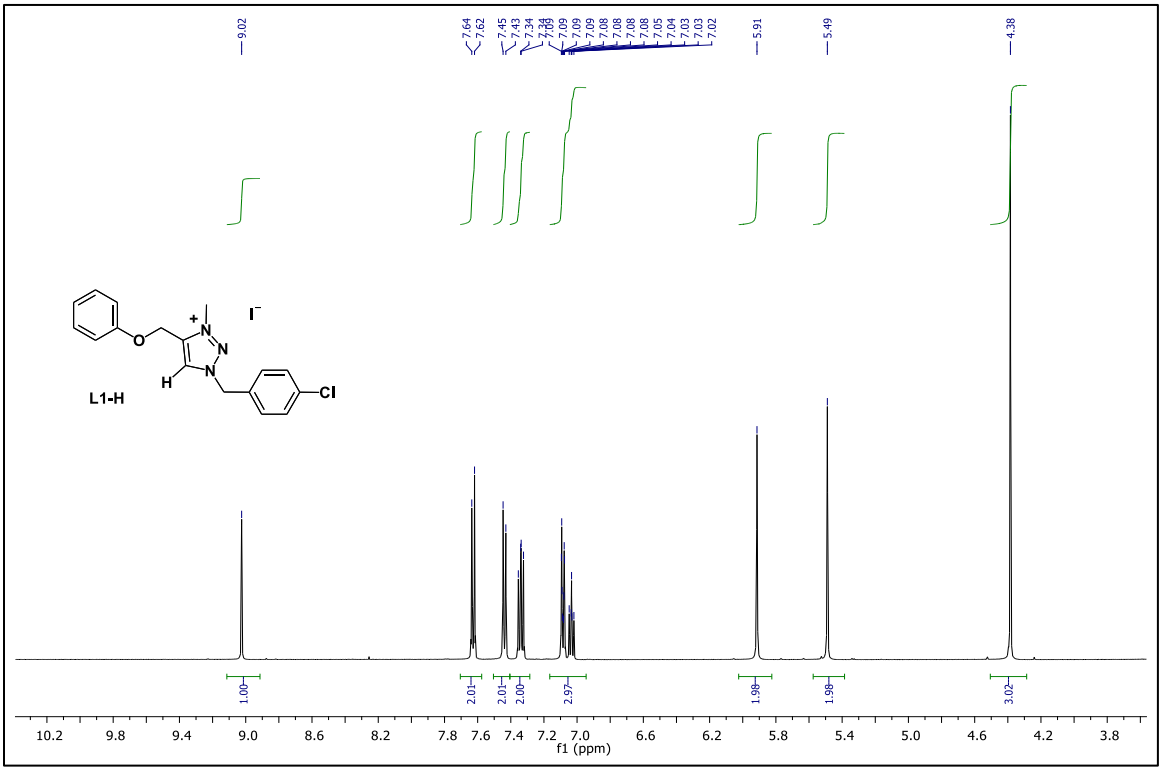

Figure S1. ^{1}H NMR (400 MHz) spectrum for **L1**-H in DMSO-$d_{6.}$

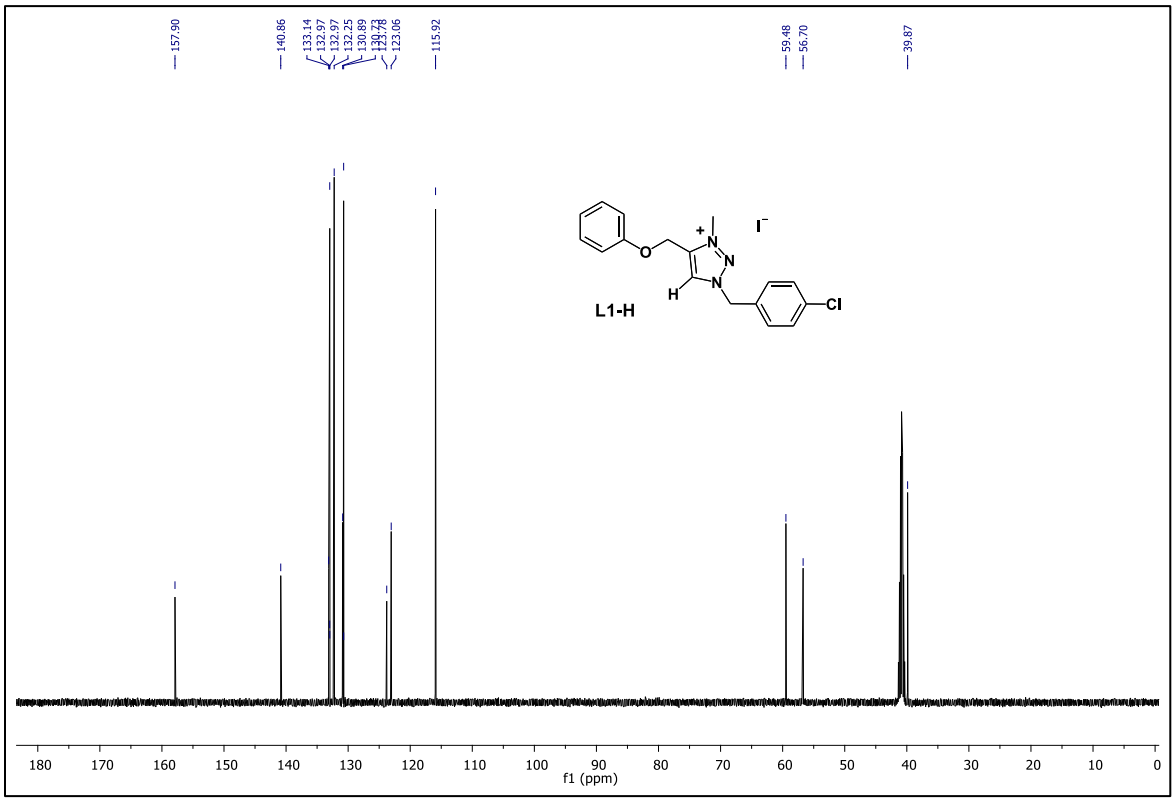

Figure S2. ^{13}C NMR (100 MHz) spectrum for **L1**-H in DMSO-d_6

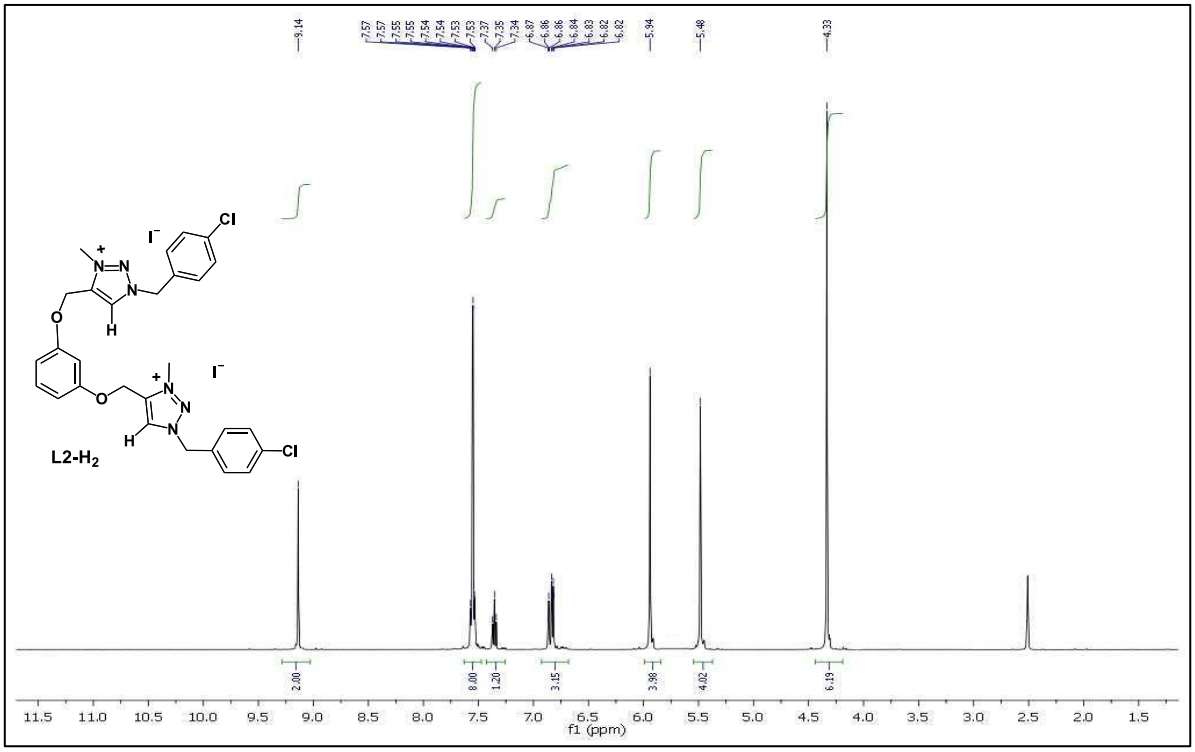

Figure S3. ^{1}H NMR (400 MHz) spectrum for **L2**-H_2 in DMSO-d_6

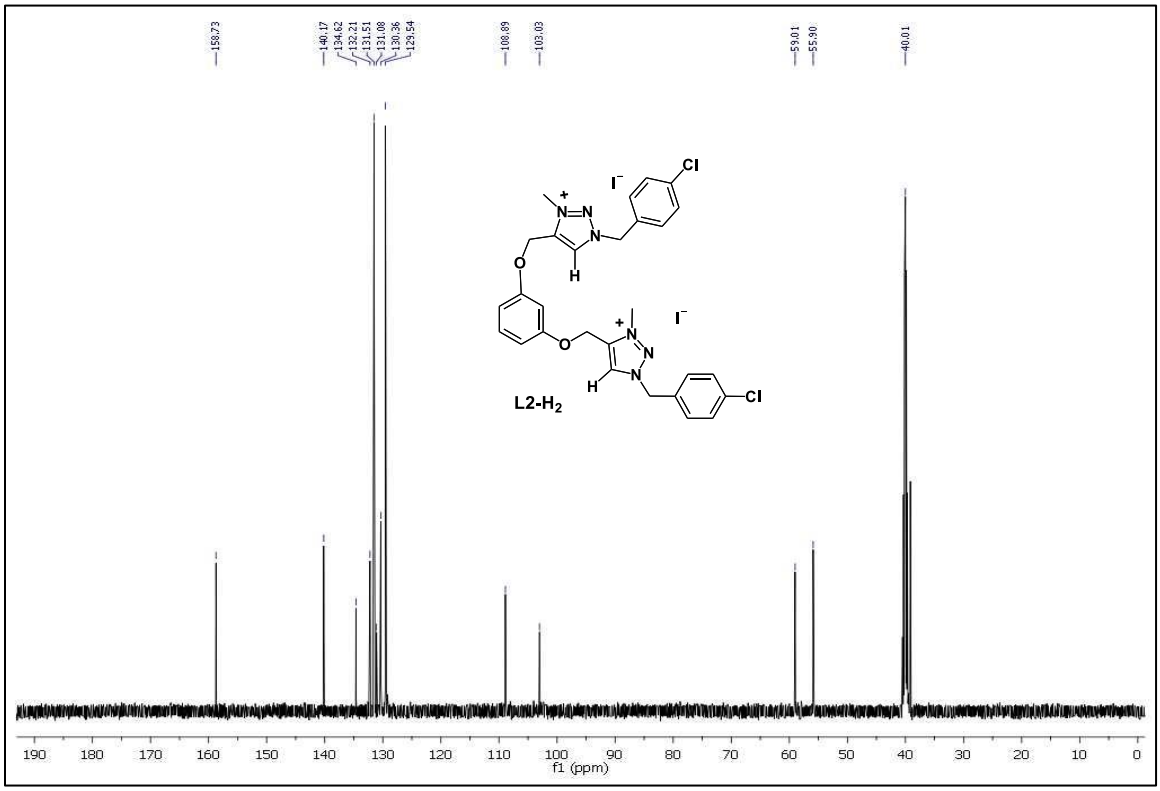

Figure S4. ^{13}C NMR (100 MHz) spectrum for **L2**-H_2 in DMSO-d_6

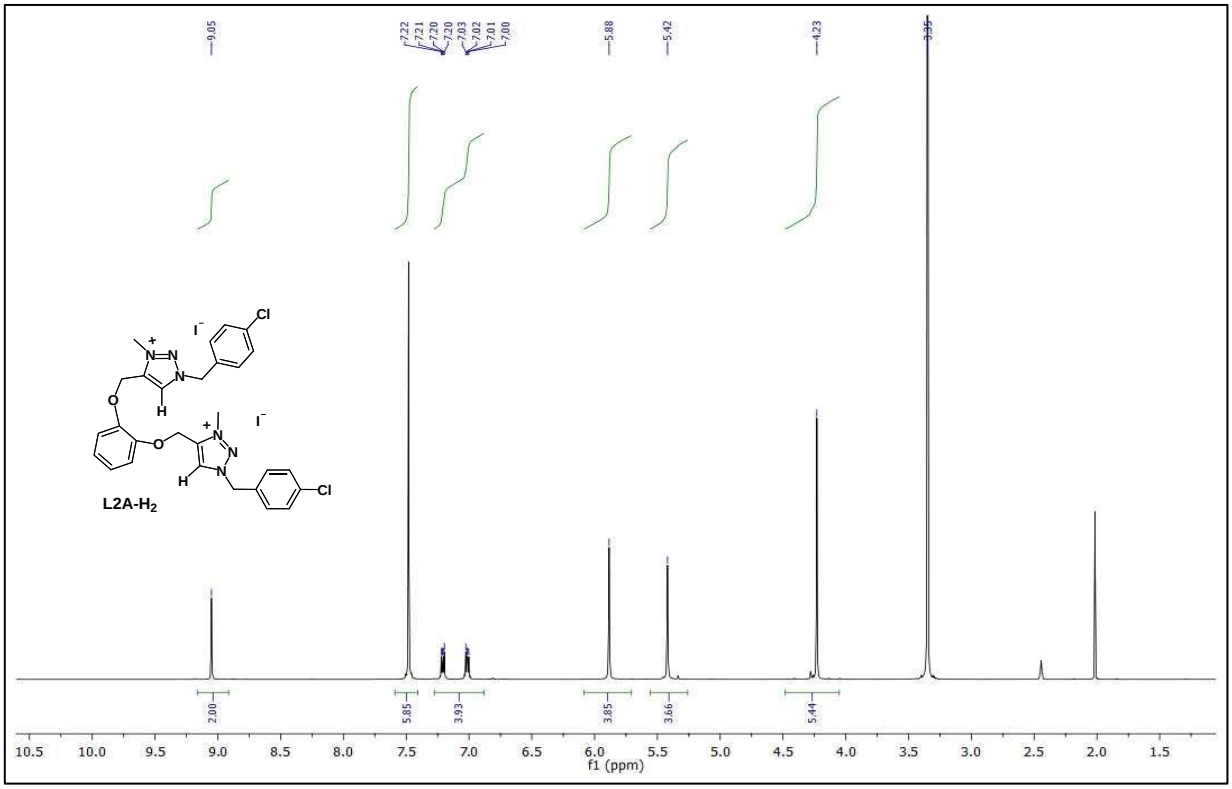

Figure S5. ^{1}H NMR (400 MHz) spectrum for **L2A**-H_2 in DMSO-d_6

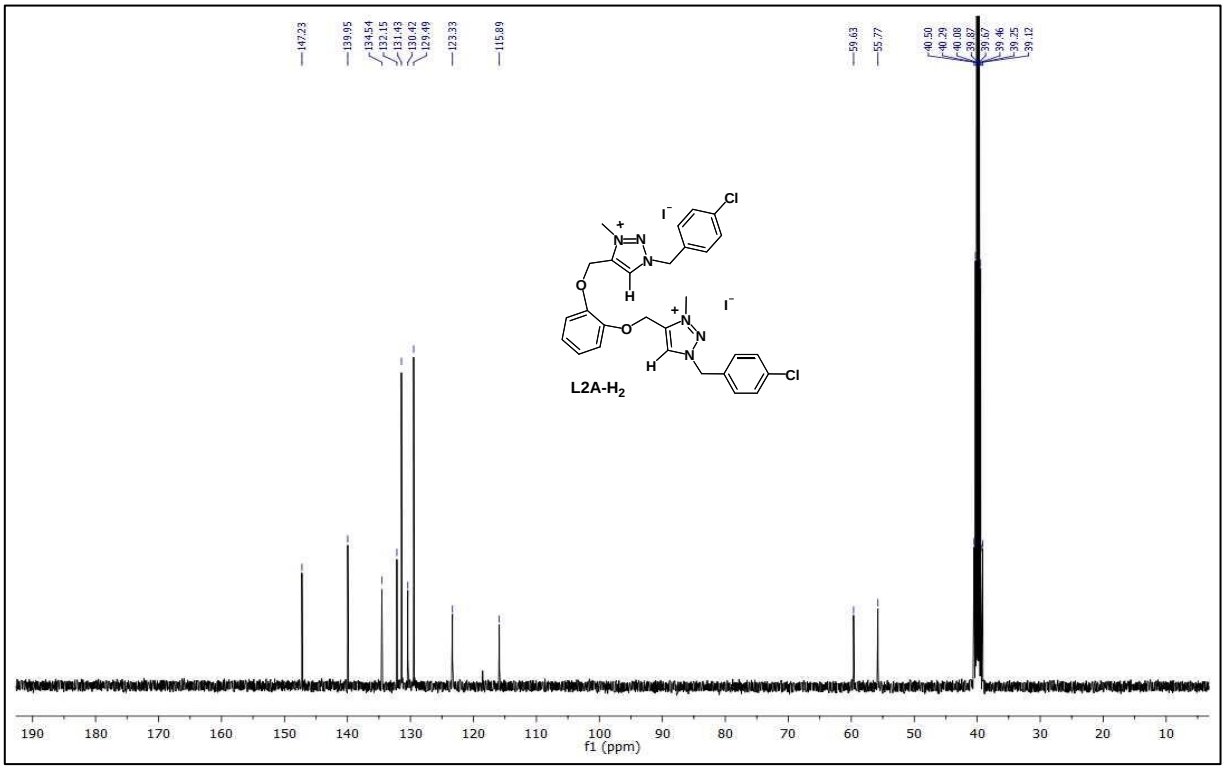

Figure S6. ^{13}C NMR (100 MHz) spectrum for **L2A**-H_2 in DMSO-d_6

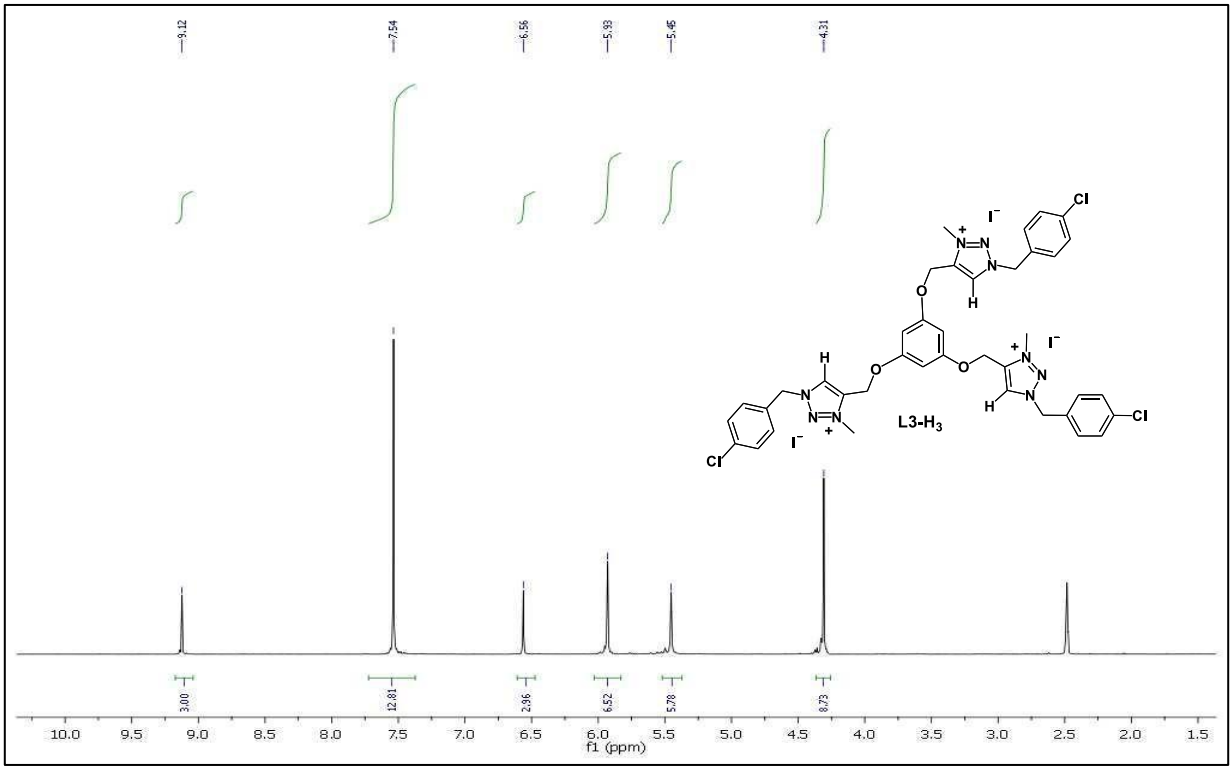

Figure S7. ^{1}H NMR (400 MHz) spectrum for **L3**-H_3 in DMSO-d_6

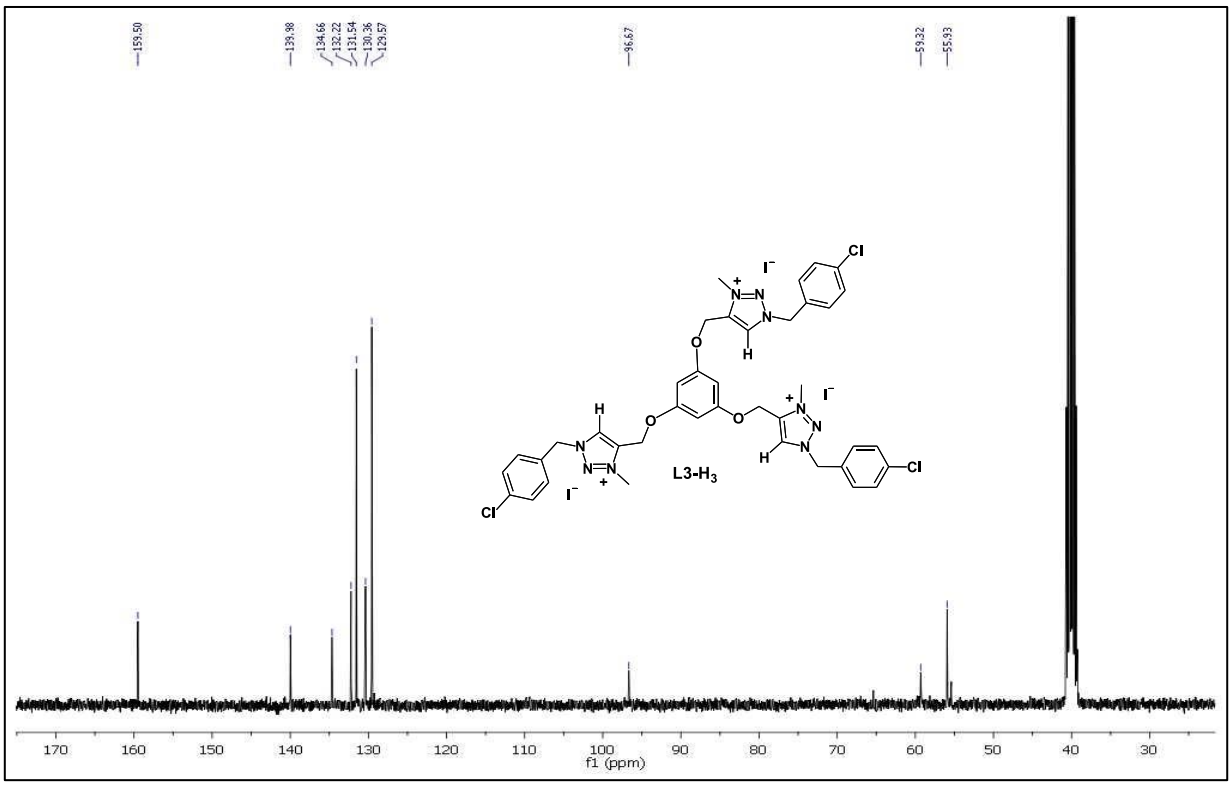

Figure S8. ^{13}C NMR (100 MHz) spectrum for **L3**-H_3 in DMSO-d_6

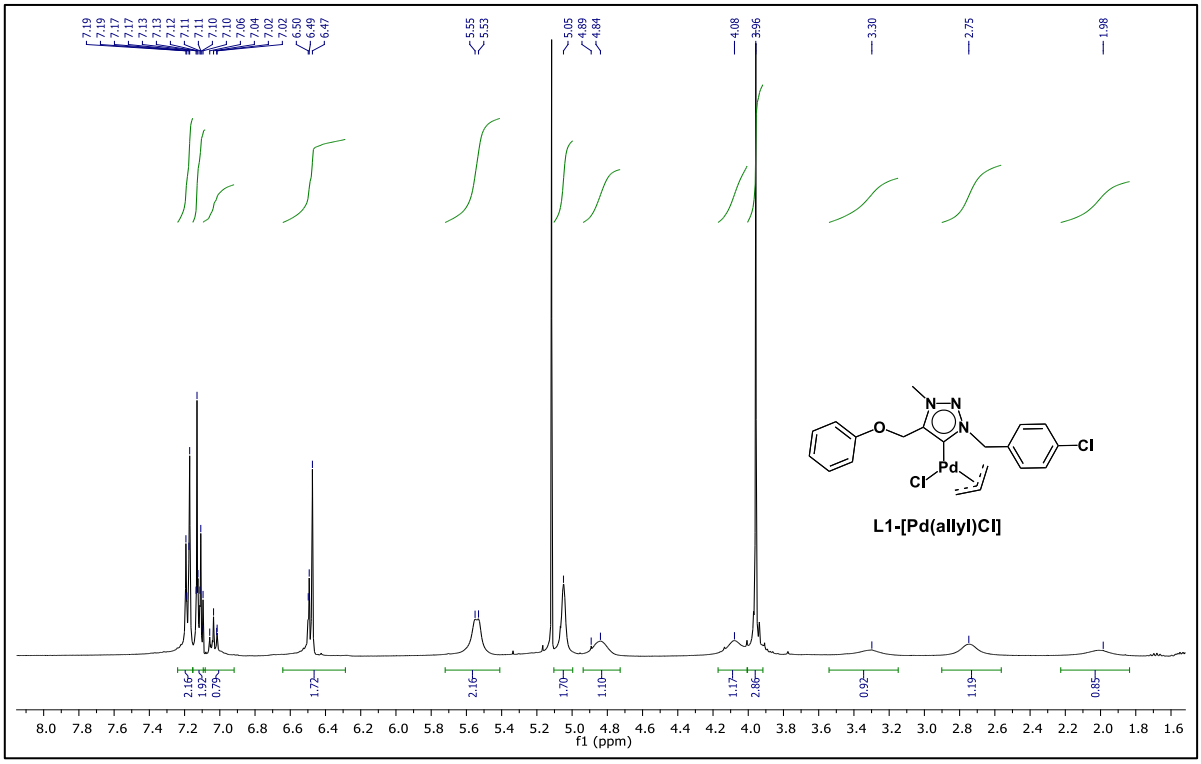

Figure S9. ^{1}H NMR (400 MHz) spectrum for **L1**-[Pd(allyl)Cl] in$CDCl_3$

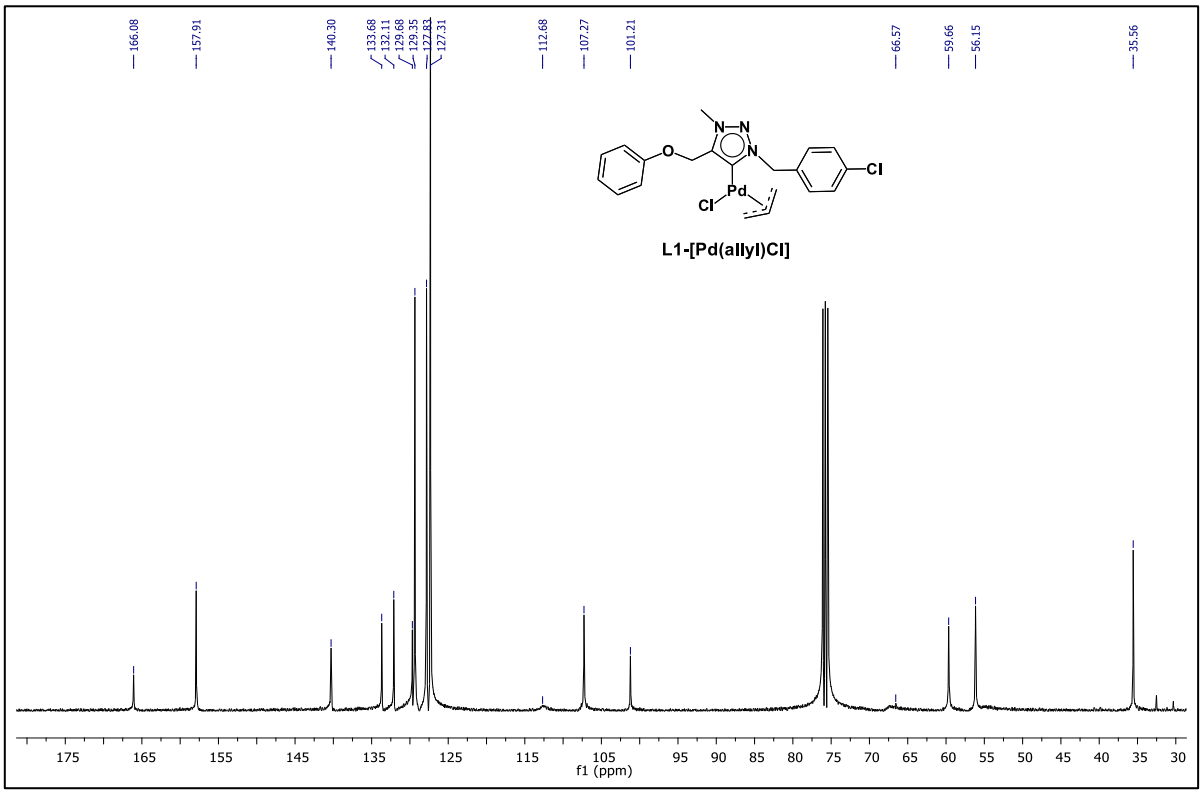

Figure S10. ^{13}C NMR (100 MHz) spectrum for **L1**-[Pd(allyl)Cl] in $CDCl_3$

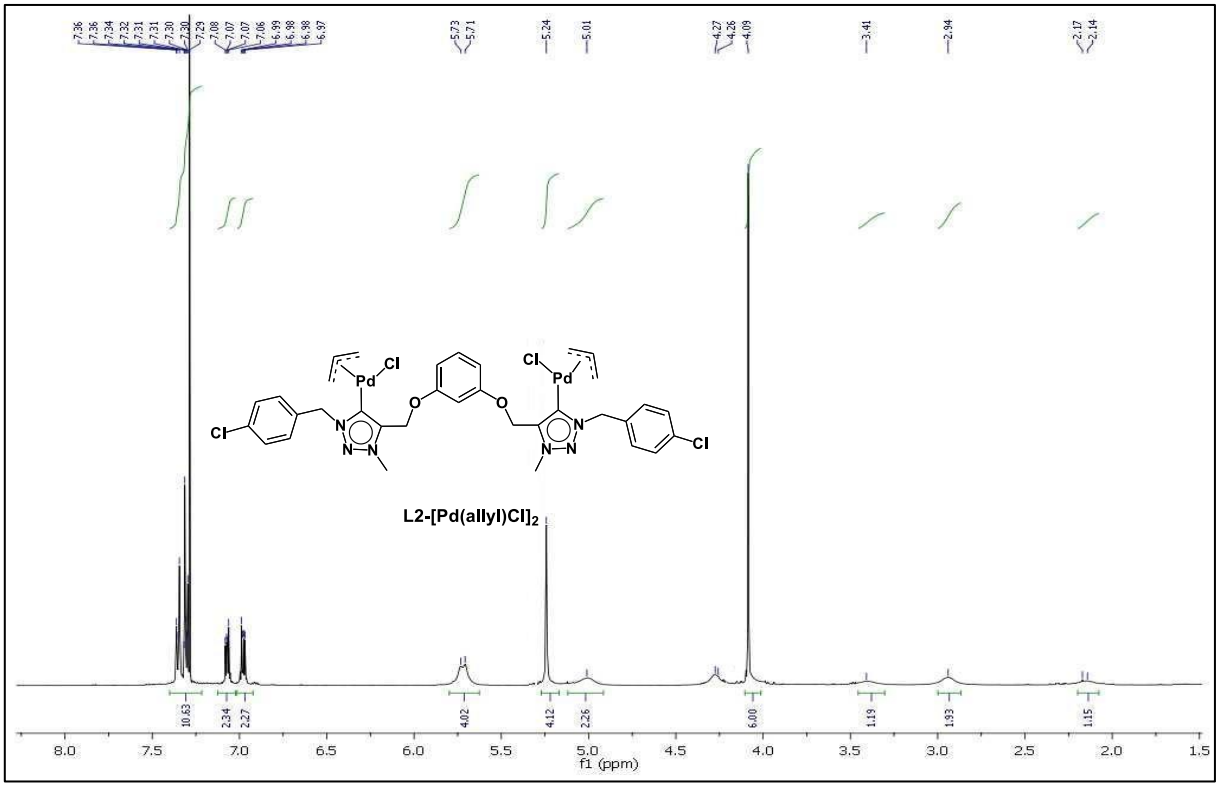

Figure S11. ^{1}H NMR (400 MHz) spectrum for **L2**-[Pd(allyl)Cl]$_2$ in$CDCl_3$

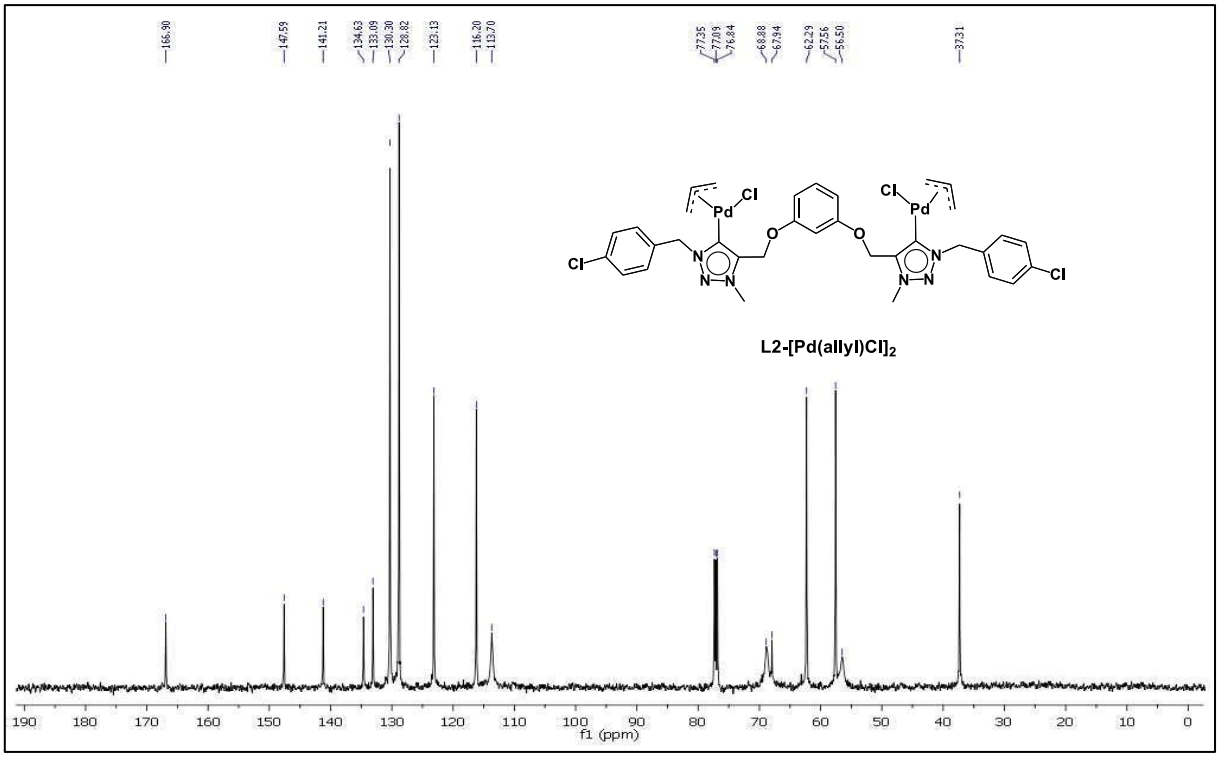

Figure S12. ^{13}C NMR (100 MHz) spectrum for **L2**-[Pd(allyl)Cl]$_2$ in $CDCl_3$

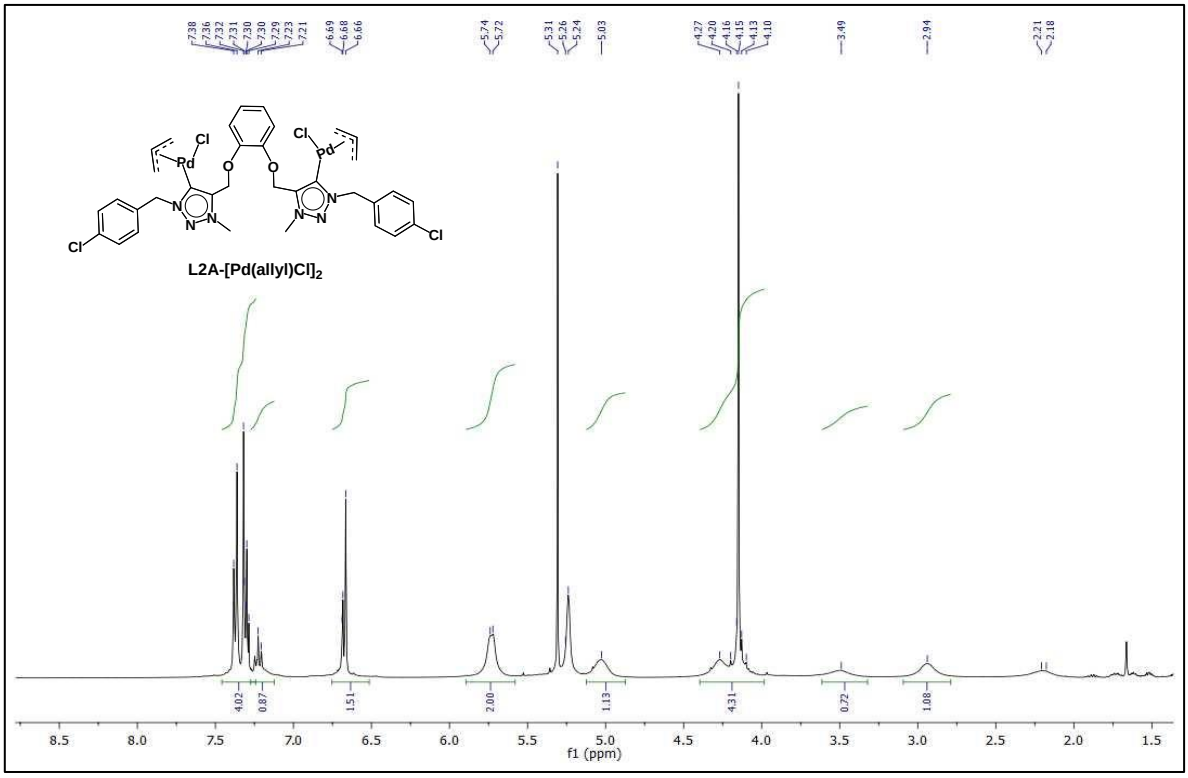

Figure S13. ^{1}H NMR (400 MHz) spectrum for **L2A**-[Pd(allyl)Cl]$_2$ in$CDCl_3$

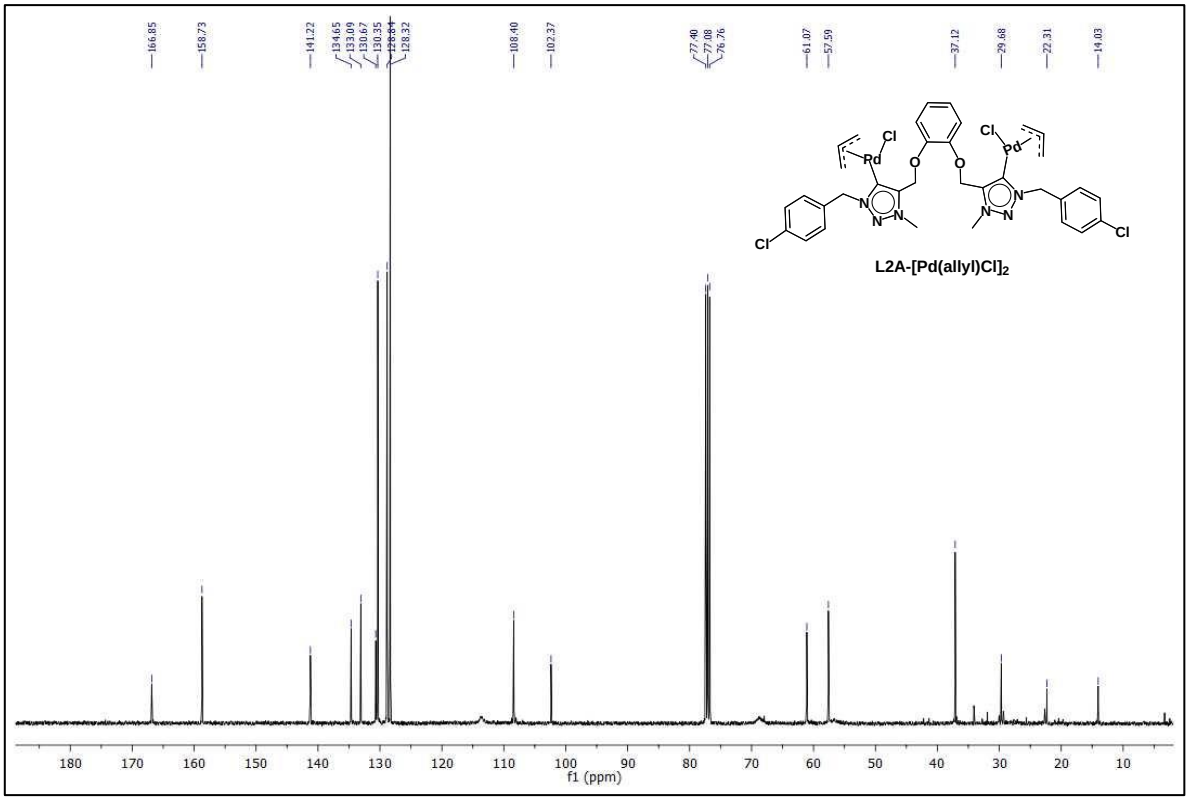

Figure S14. ^{13}C NMR (100 MHz) spectrum for **L2A**-[Pd(allyl)Cl]$_2$ in $CDCl_3$

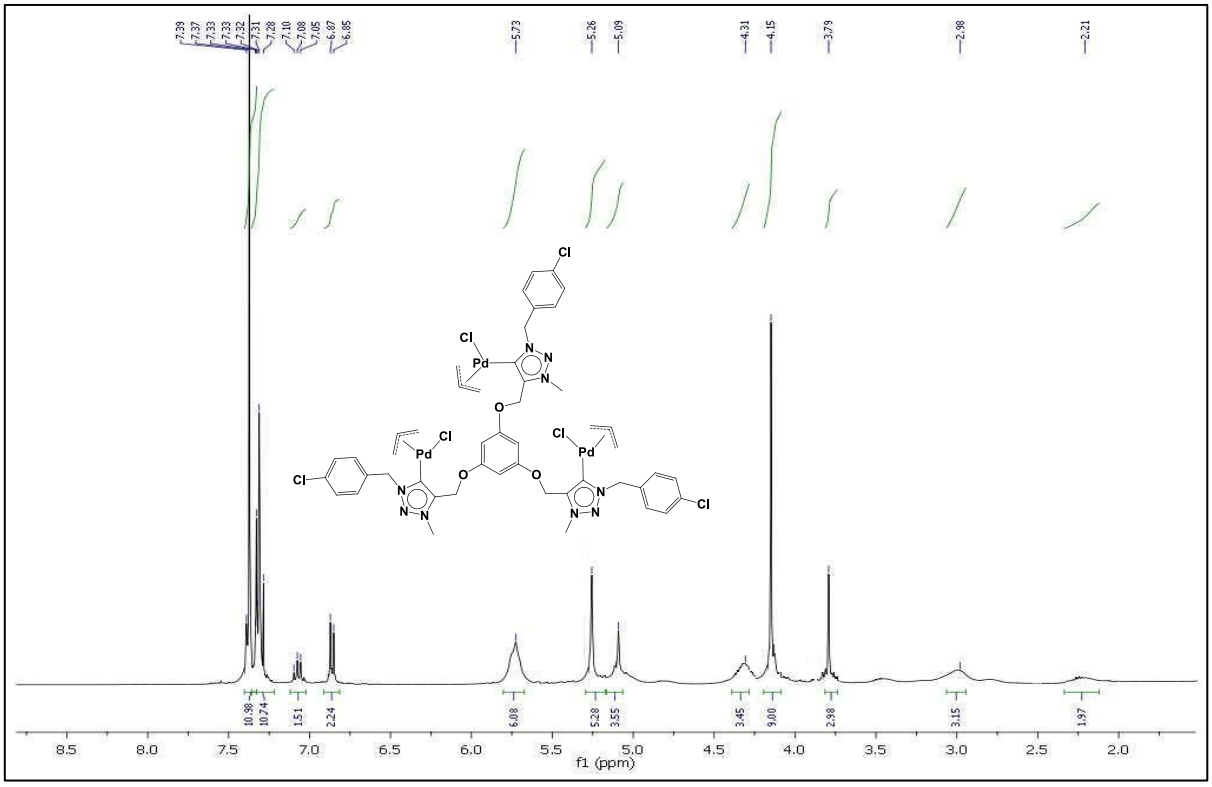

Figure S15. ^{1}H NMR (400 MHz) spectrum for **L3**-[Pd(allyl)Cl]$_3$ in$CDCl_3$

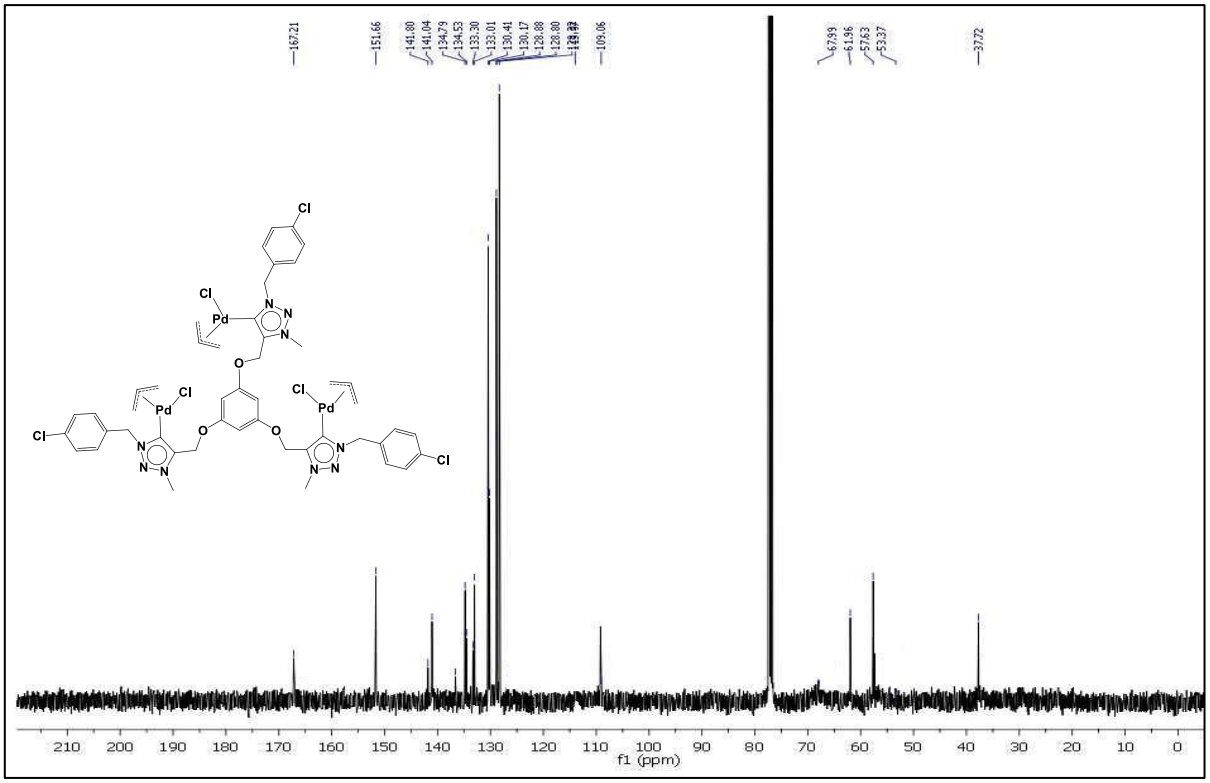

Figure S16. ^{13}C NMR (100 MHz) spectrum for **L2A**-[Pd(allyl)Cl]$_2$ in $CDCl_3$

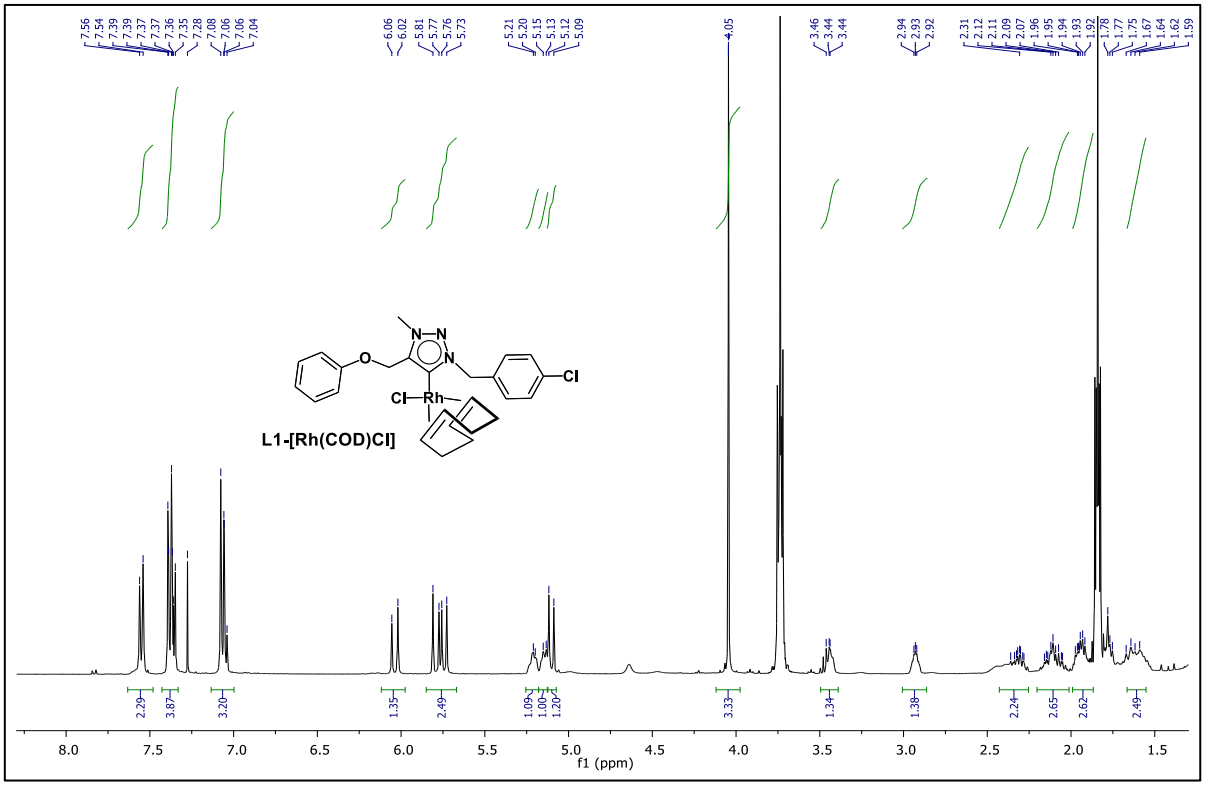

Figure S17. ^{1}H NMR (400 MHz) spectrum for **L1**-[Rh(COD)Cl] in$CDCl_3$

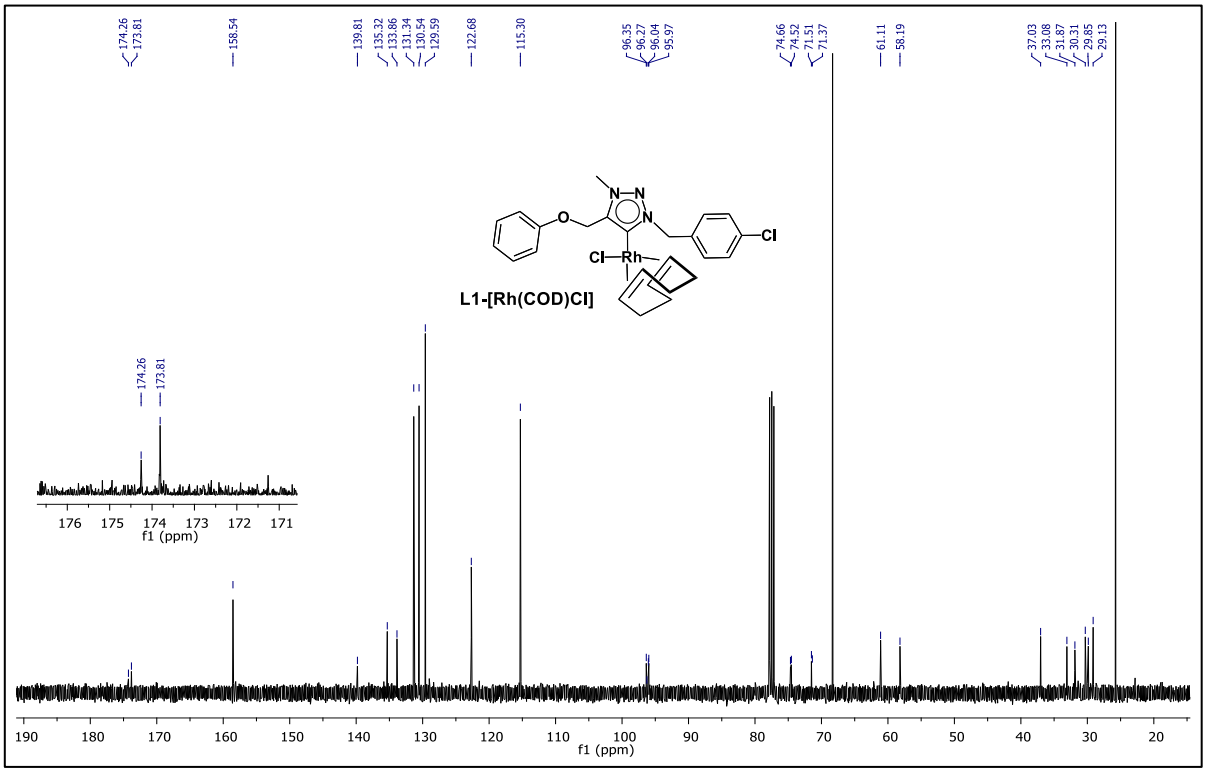

Figure S18. ^{13}C NMR (100 MHz) spectrum for **L1**-[Rh(COD)Cl] in $CDCl_3$

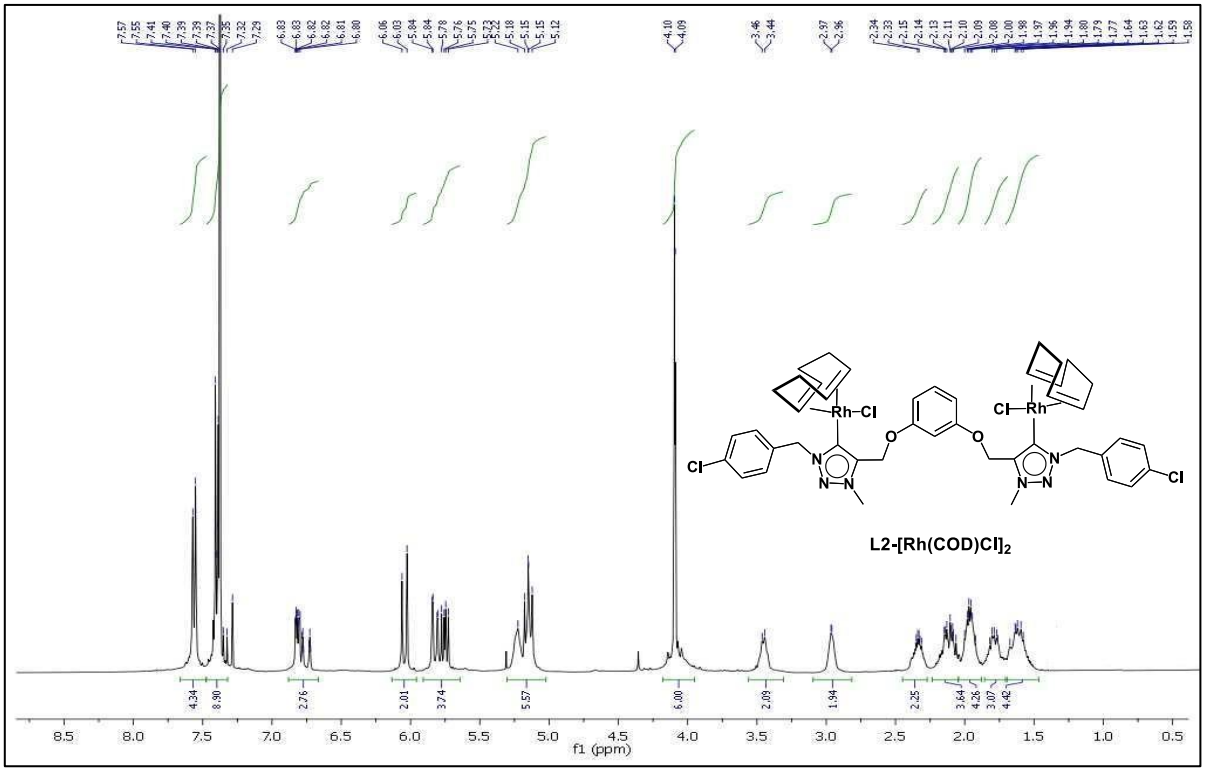

Figure S19. ^{1}H NMR (400 MHz) spectrum for **L2**-[Rh(COD)Cl]$_2$ inCDCl$_3$

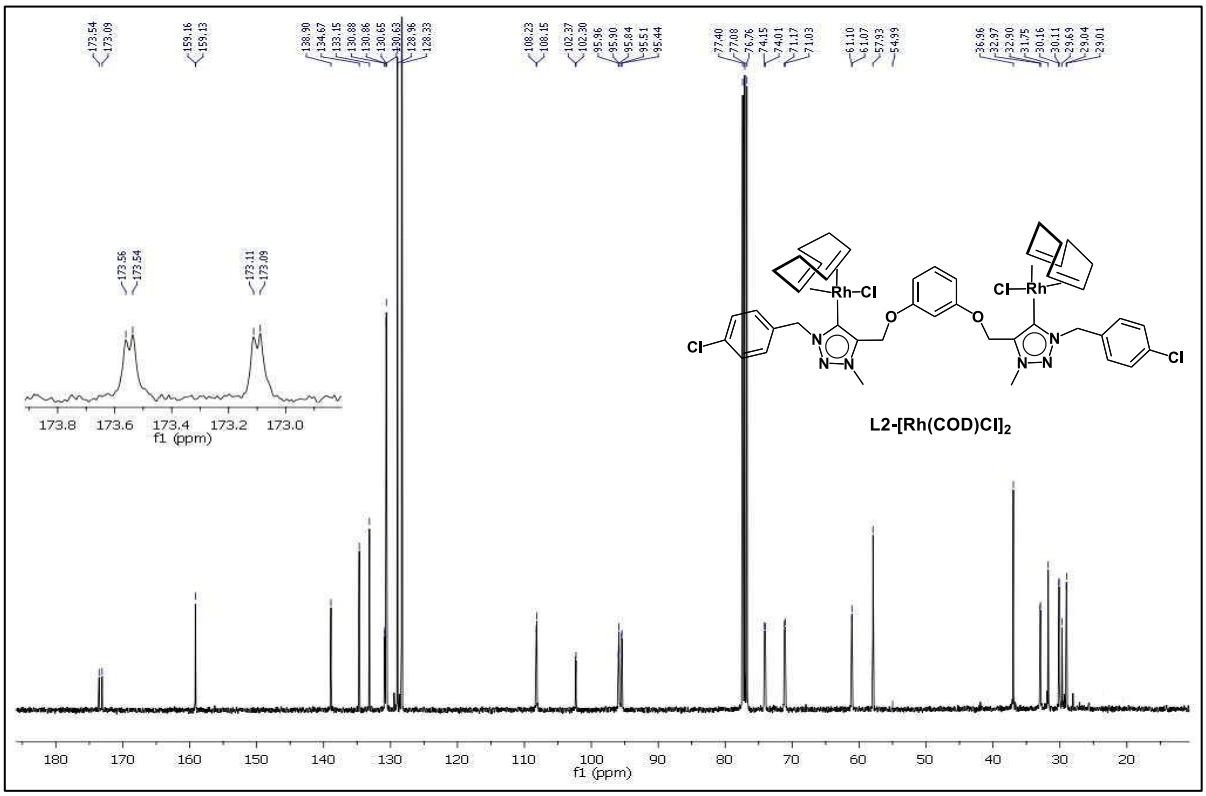

Figure S20. ^{13}C NMR (100 MHz) spectrum for **L2**-[Rh(COD)Cl]$_2$ in CDCl$_3$

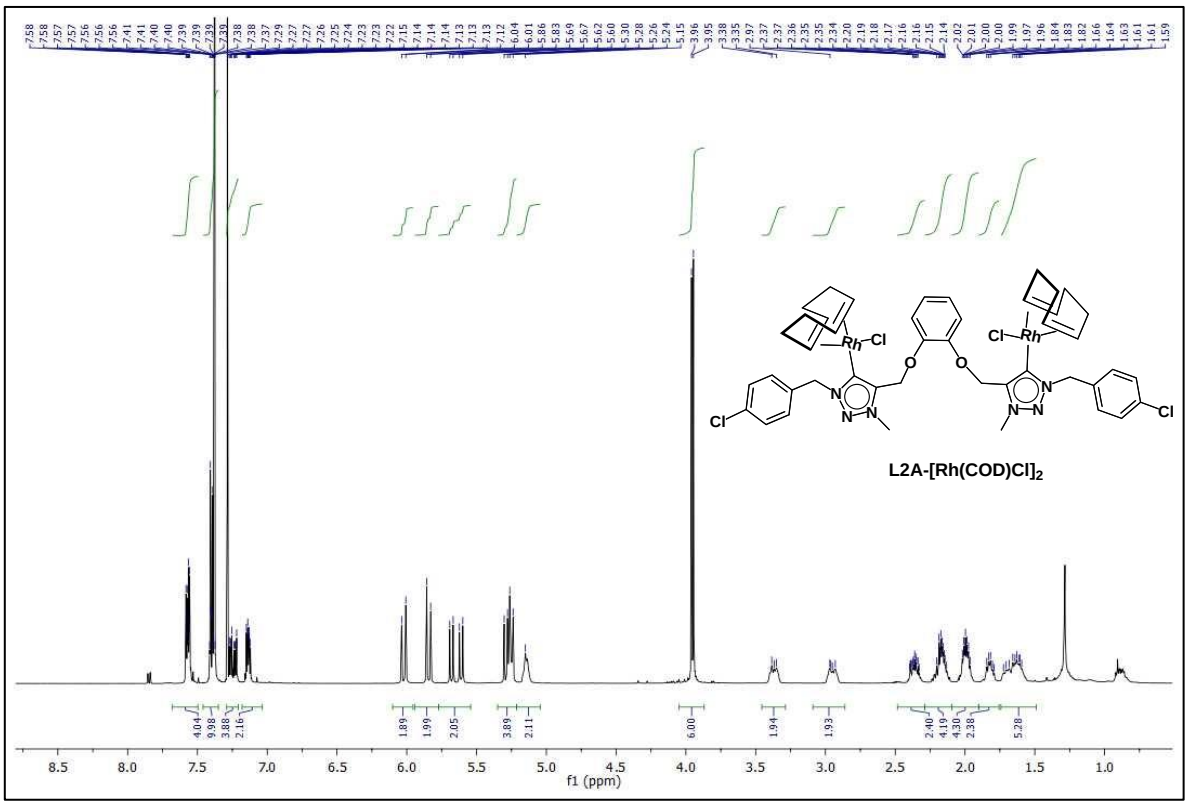

Figure S21. ^{1}H NMR (400 MHz) spectrum for **L2A**-[Rh(COD)Cl]$_2$ in$CDCl_3$

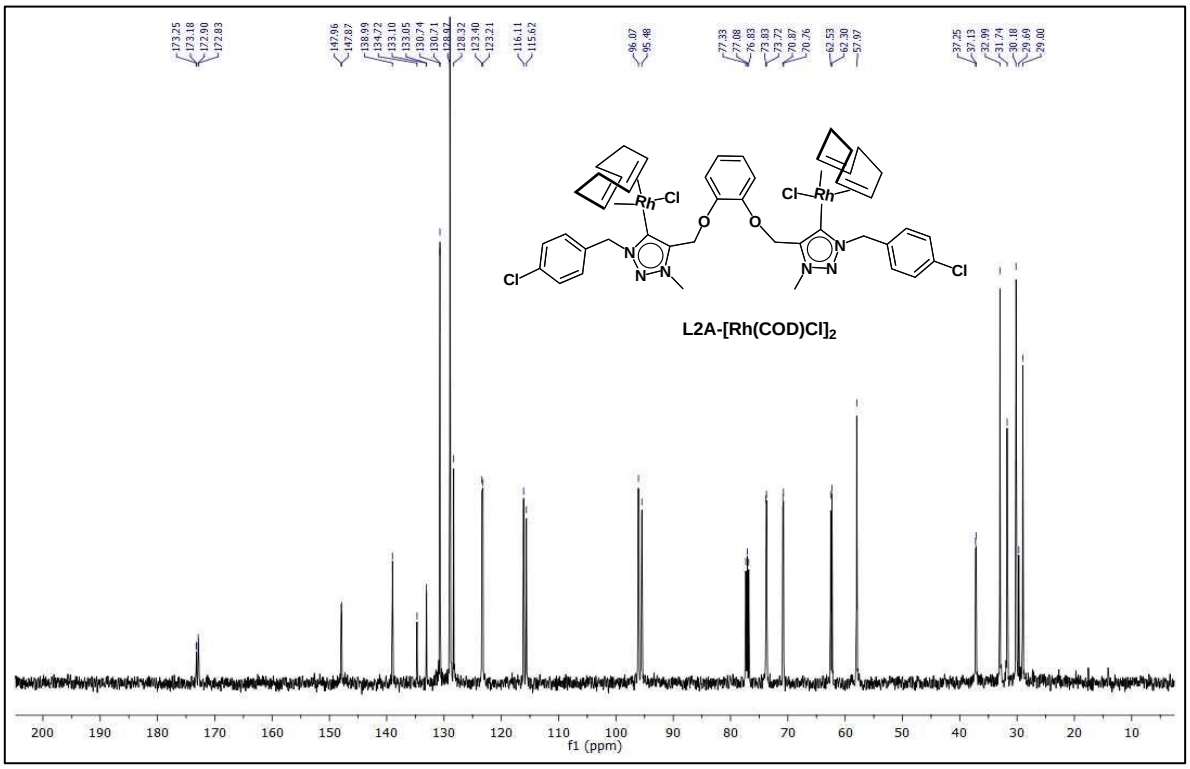

Figure S22. ^{13}C NMR (100 MHz) spectrum for **L2A**-[Rh(COD)Cl]$_2$ in $CDCl_3$

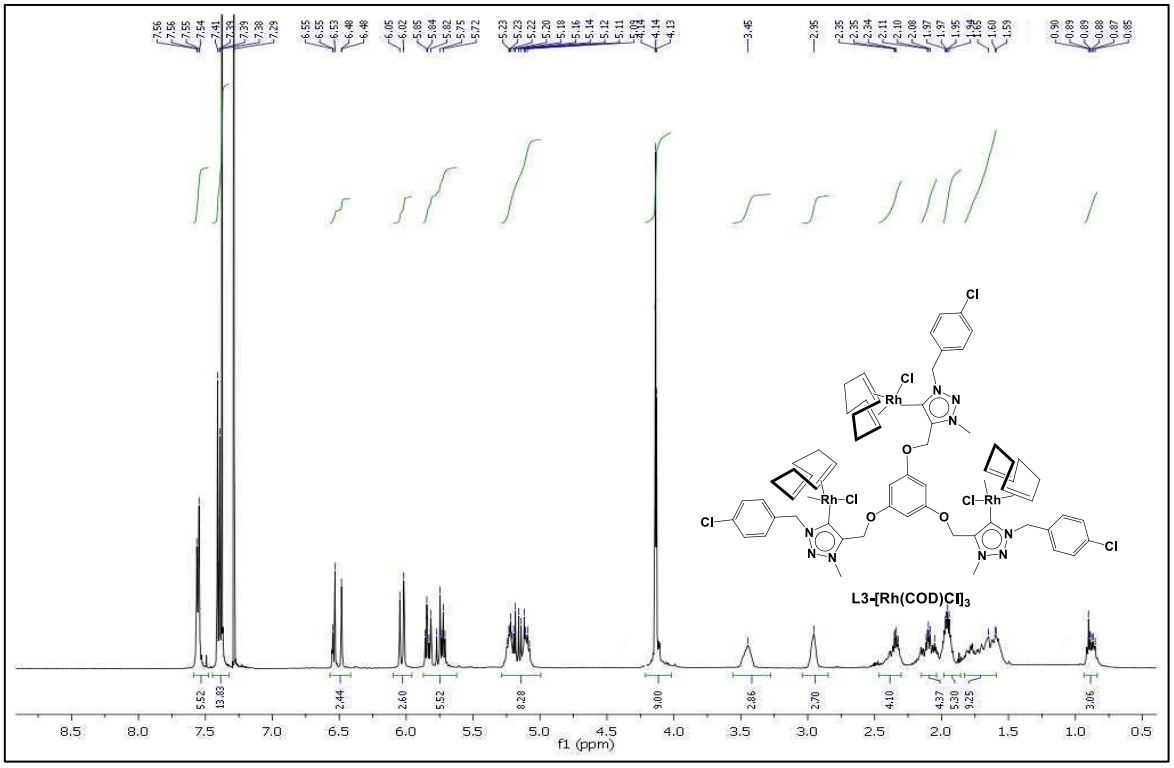

Figure S23. ^{1}H NMR (400 MHz) spectrum for **L3**-[Rh(COD)Cl]$_3$ inCDCl$_3$

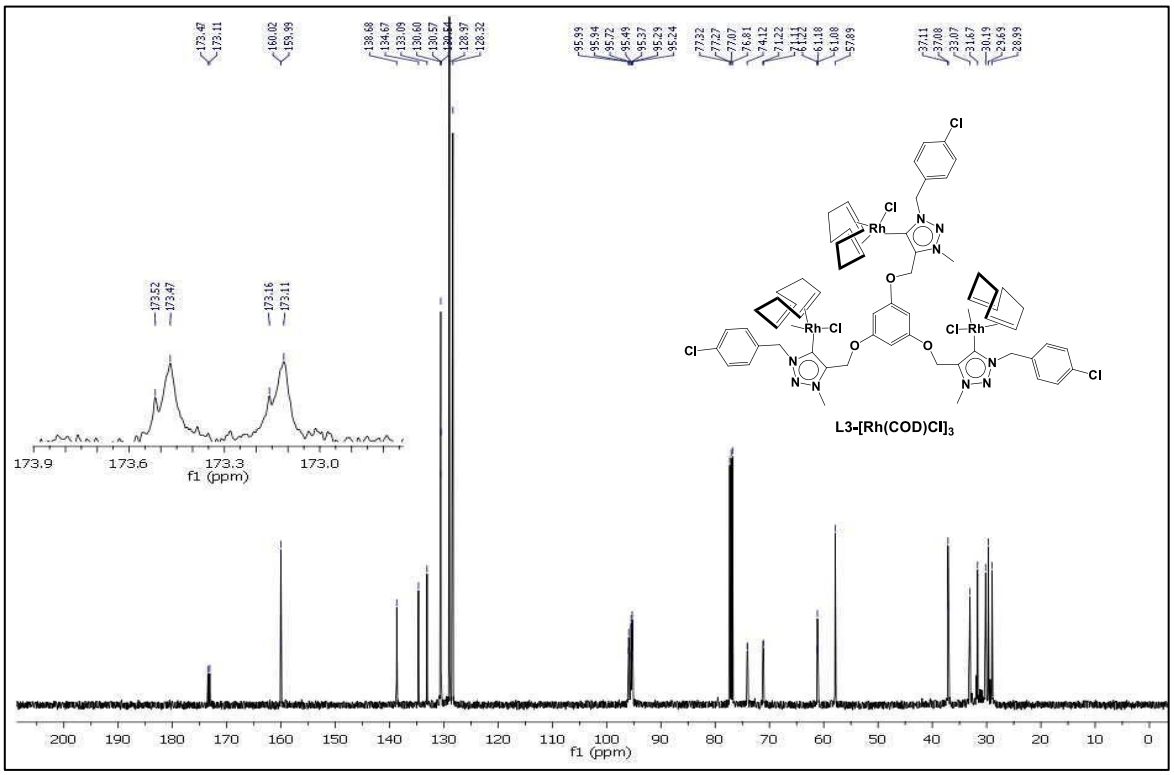

Figure S24. ^{13}C NMR (100 MHz) spectrum for **L3**-[Rh(COD)Cl]$_3$ in CDCl$_3$

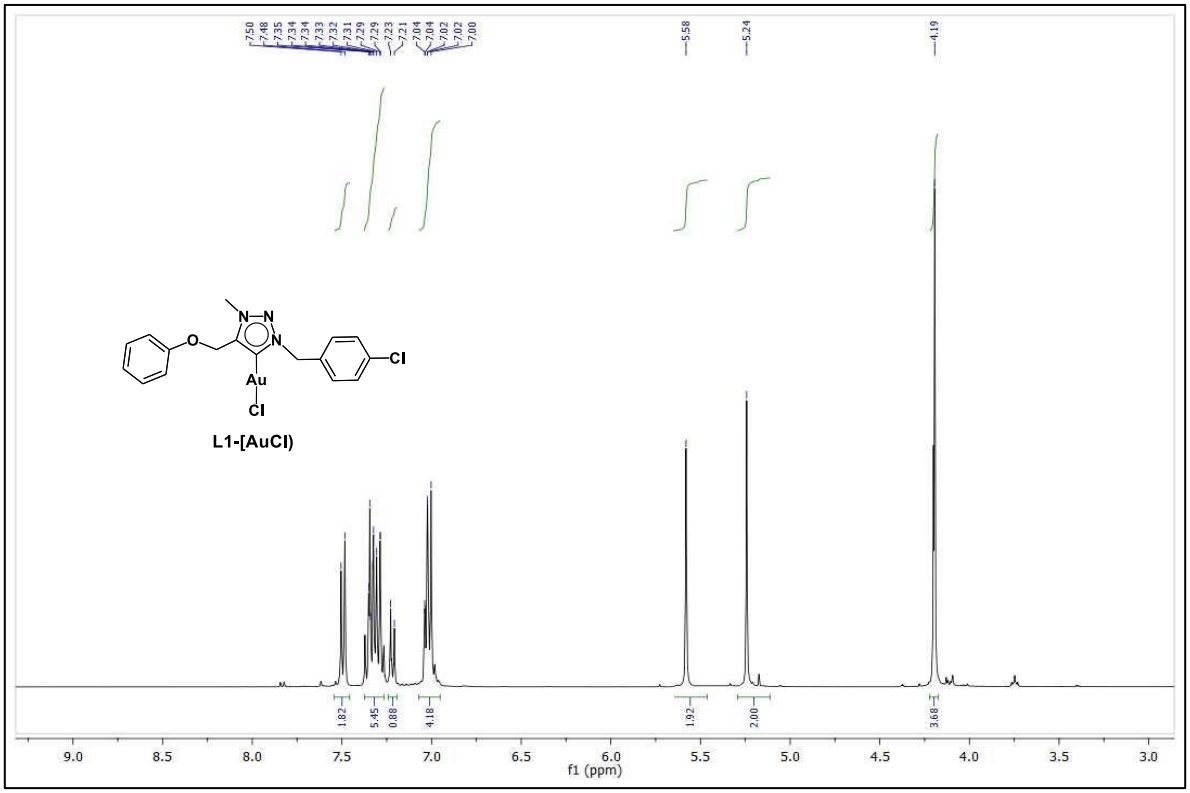

Figure S25. ^{1}H NMR (400 MHz) spectrum for **L1**-[AuCl] in$CDCl_3$

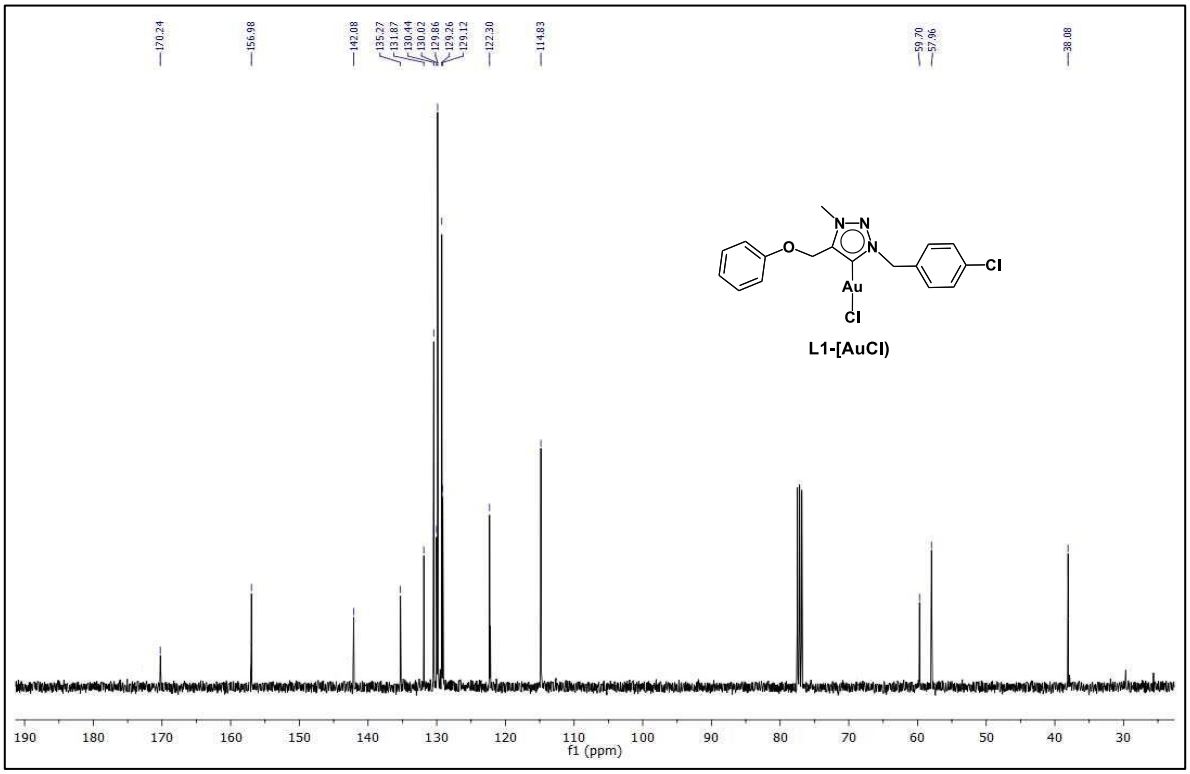

Figure S26. ^{13}C NMR (100 MHz) spectrum for **L1**-[AuCl] in $CDCl_3$

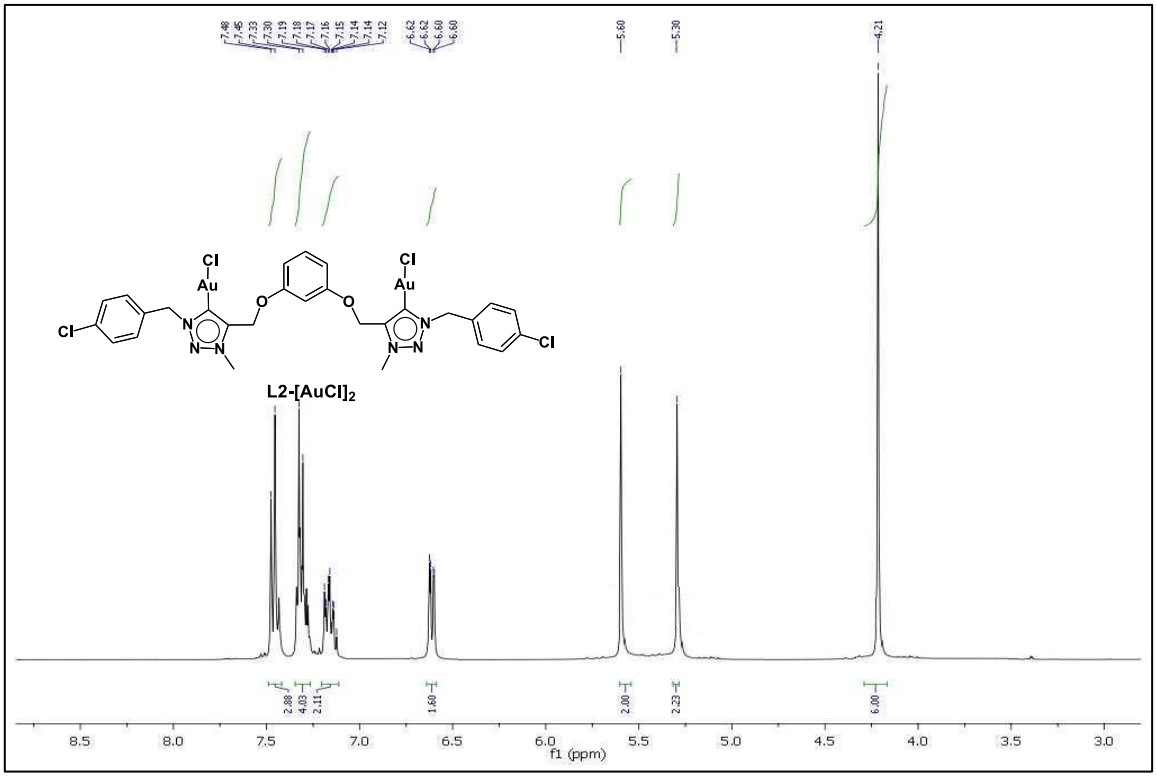

Figure S27. ^{1}H NMR (400 MHz) spectrum for **L2**-$[AuCl]_2$ in$CDCl_3$

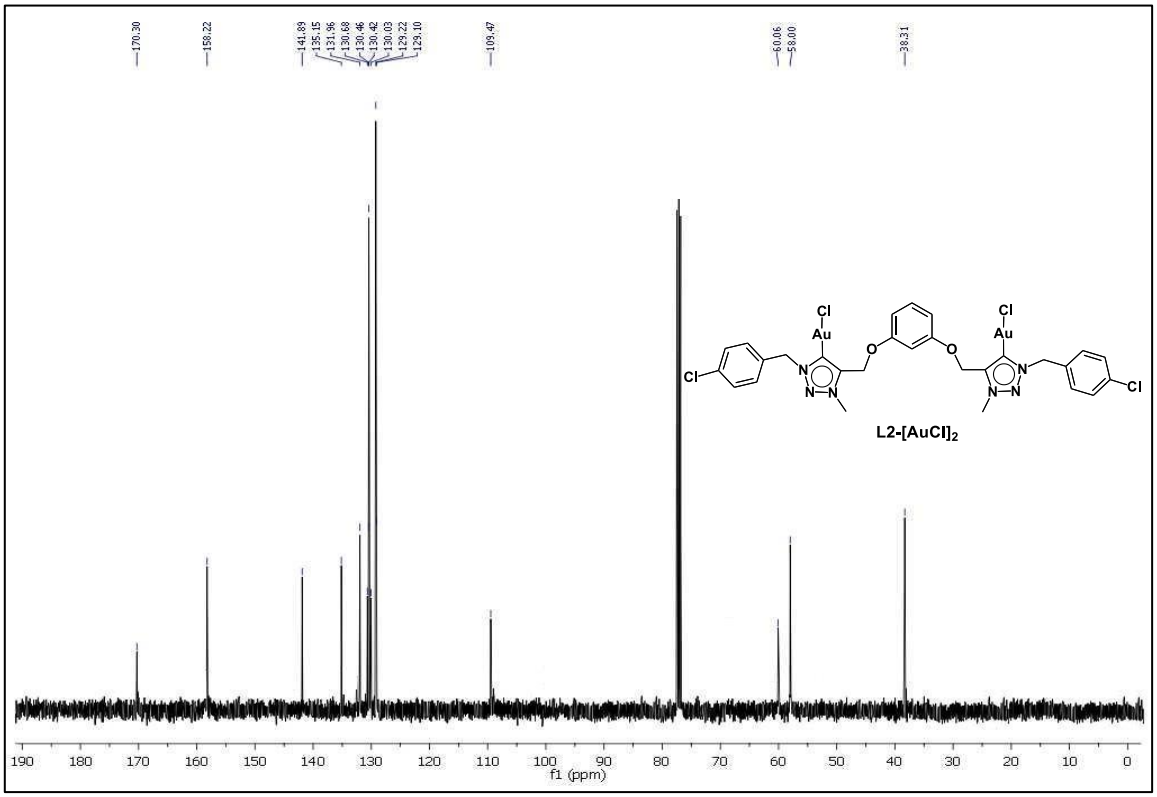

Figure S28. ^{13}C NMR (100 MHz) spectrum for **L2**-$[AuCl]_2$ in $CDCl_3$

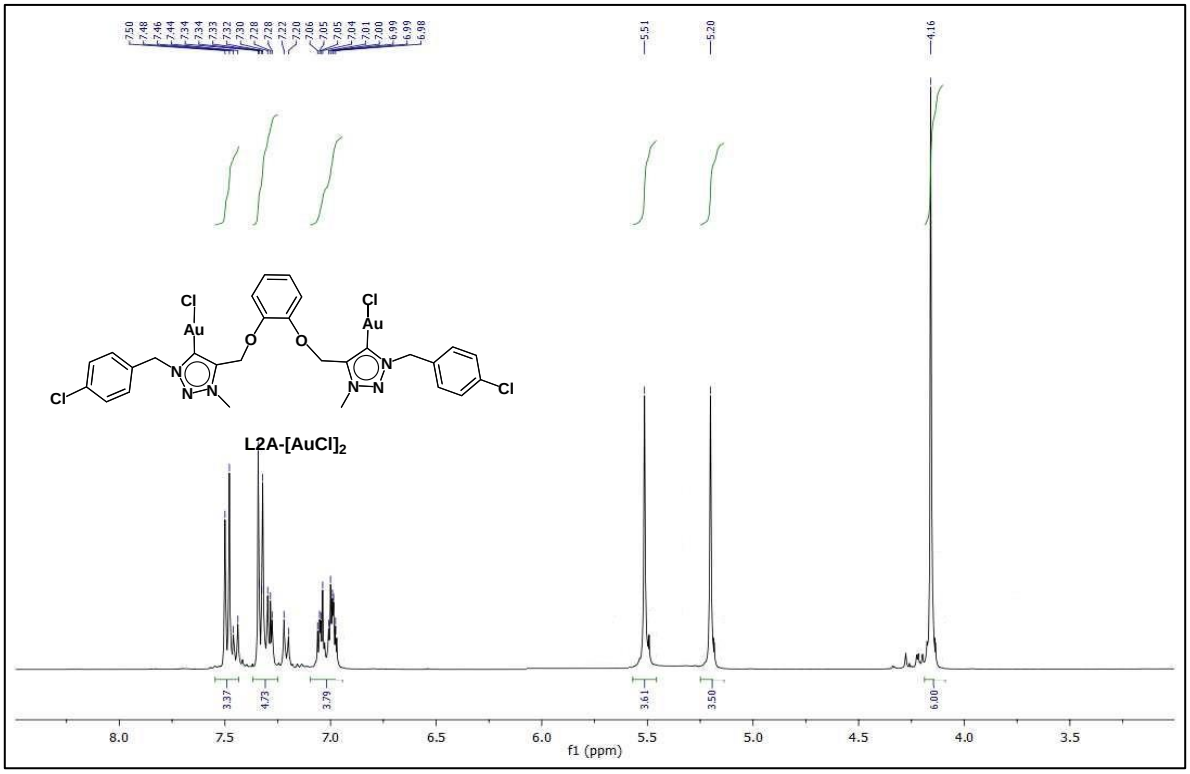

Figure S29. ^{1}H NMR (400 MHz) spectrum for **L2A**-[AuCl]$_2$ in$CDCl_3$

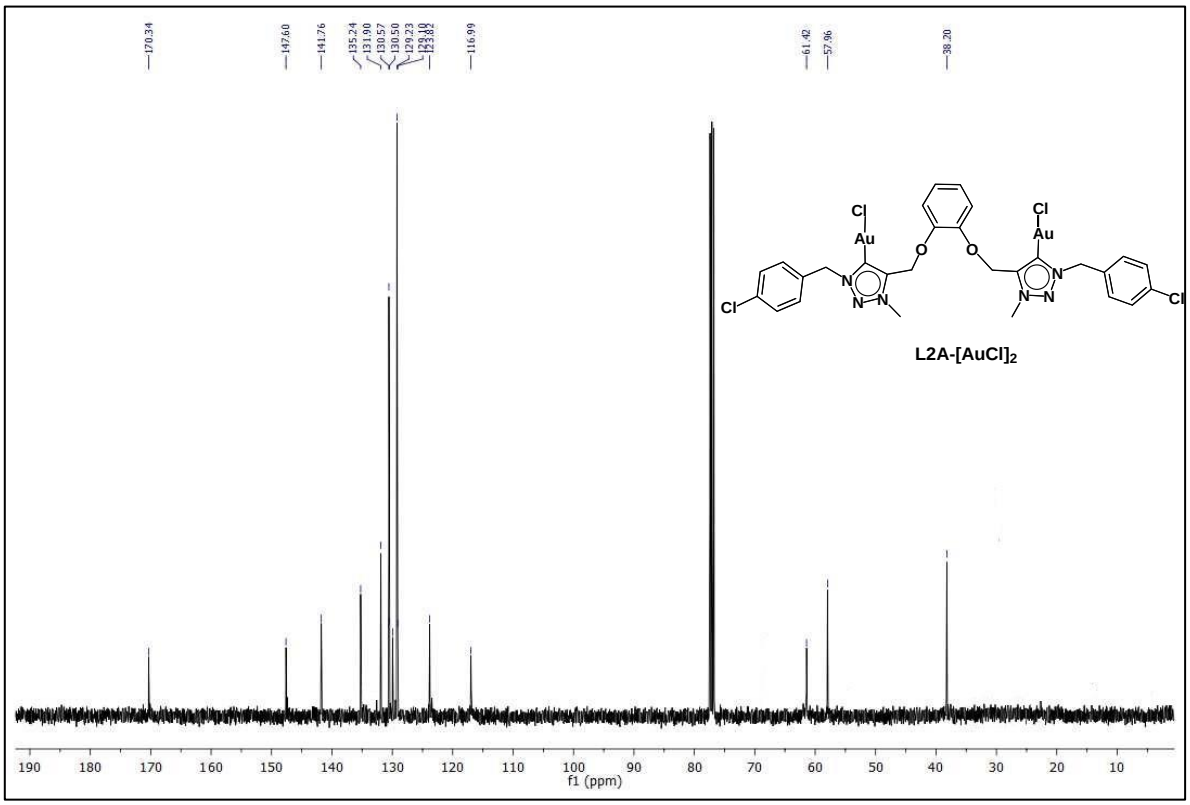

Figure S30. ^{13}C NMR (100 MHz) spectrum for **L2A**-[AuCl]$_2$ in $CDCl_3$

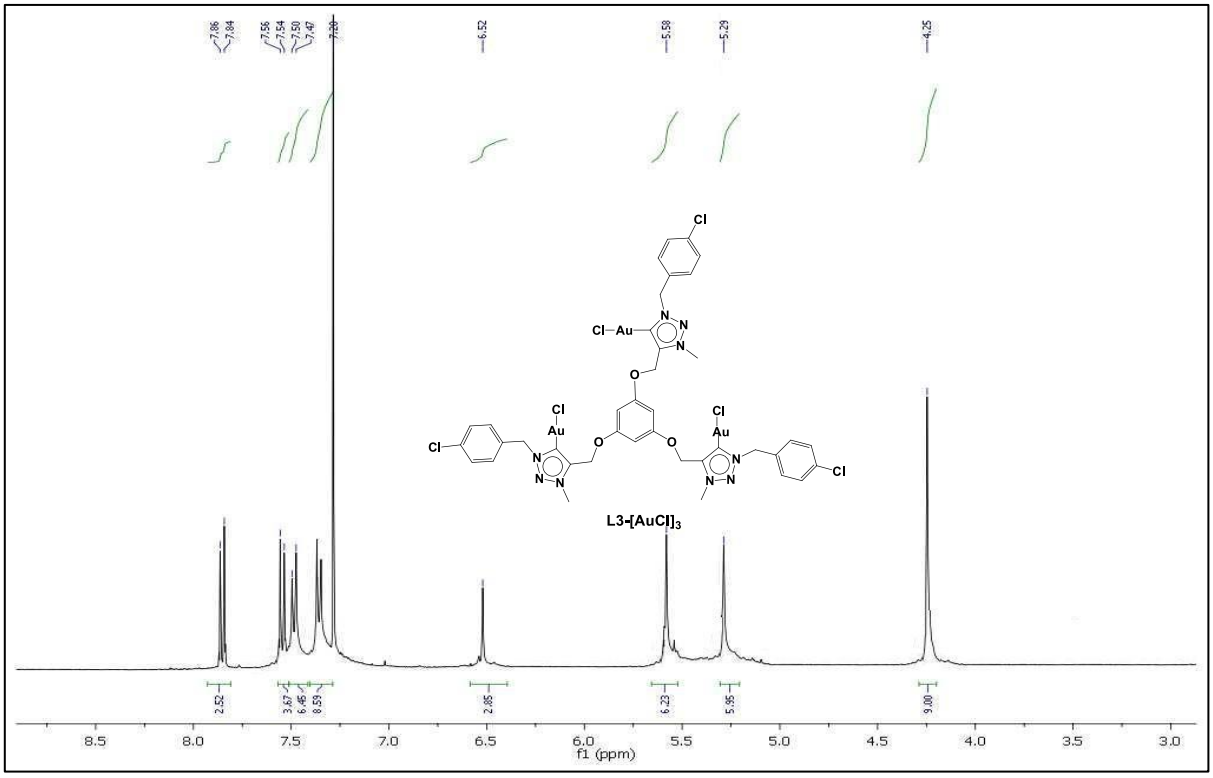

Figure S31. ^{1}H NMR (400 MHz) spectrum for **L3**-$[AuCl]_3$ in$CDCl_3$

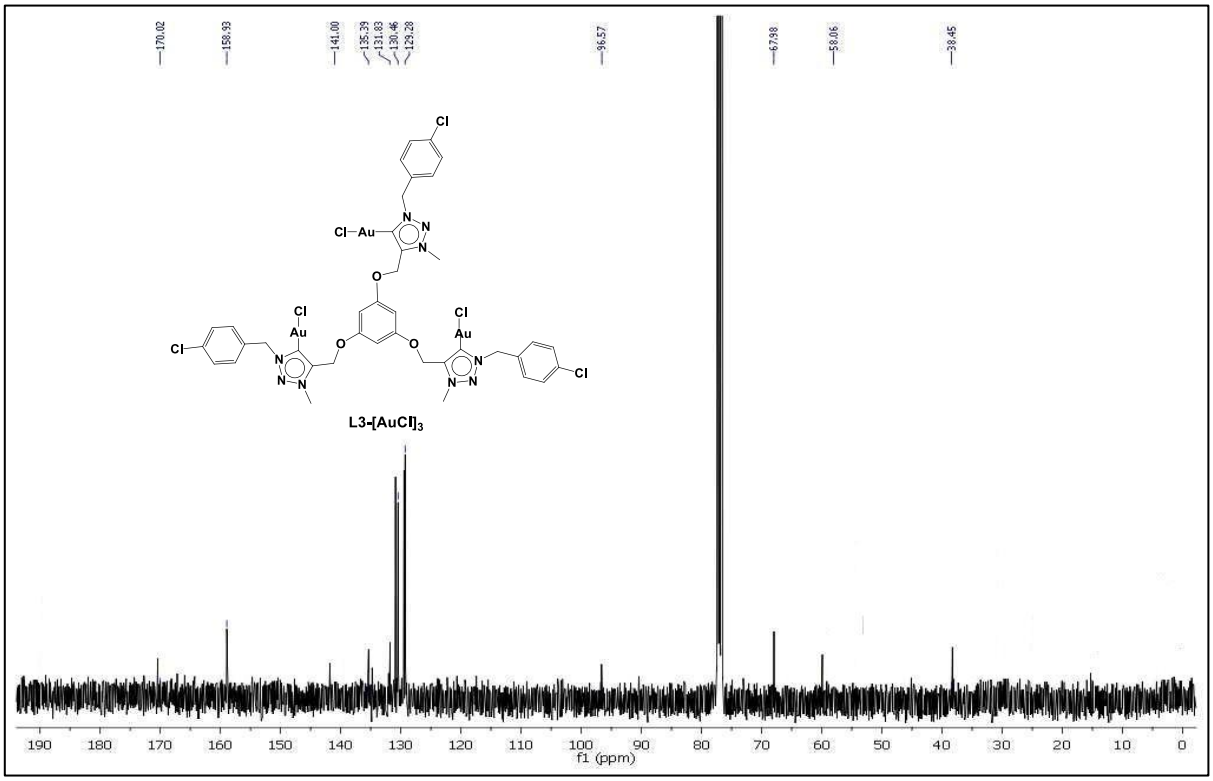

Figure S32. ^{13}C NMR (100 MHz) spectrum for **L3**-$[AuCl]_3$ in $CDCl_3$

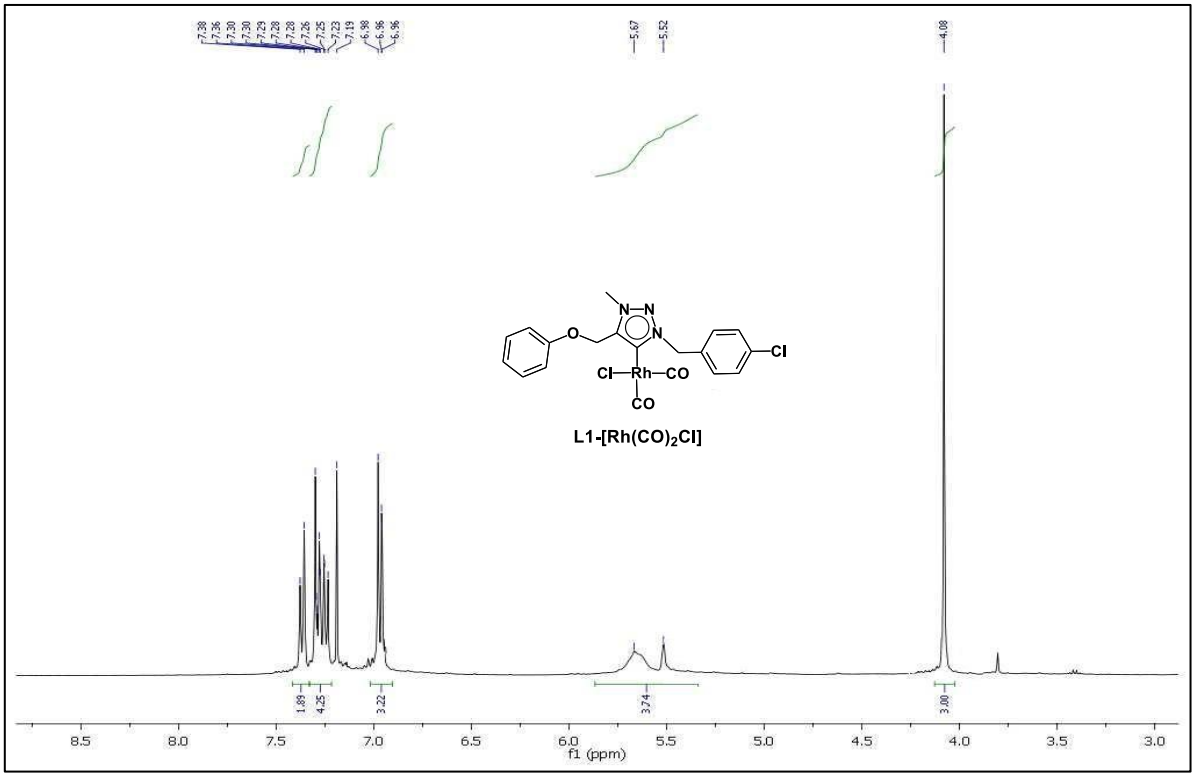

Figure S33. ^{1}H NMR (400 MHz) spectrum for **L1**-[Rh(CO)$_2$Cl] in$CDCl_3$

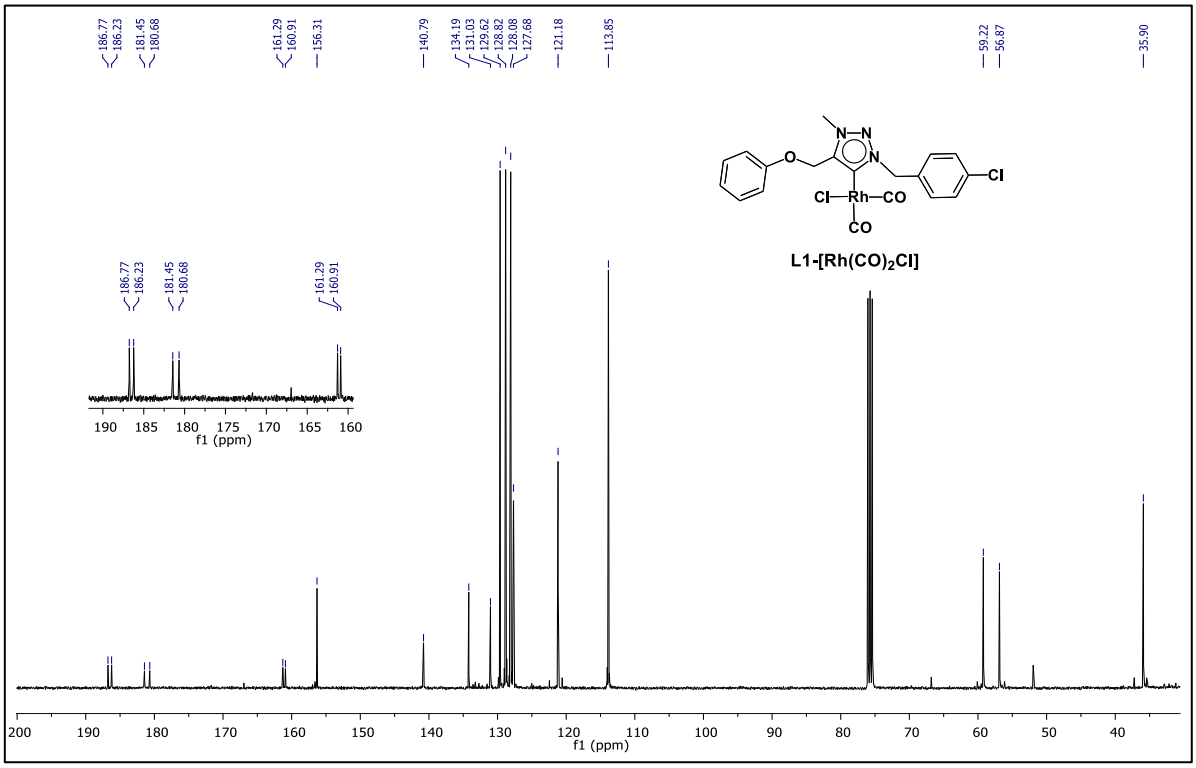

Figure S34. ^{13}C NMR (100 MHz) spectrum for **L1**-[Rh(CO)$_2$Cl] in $CDCl_3$

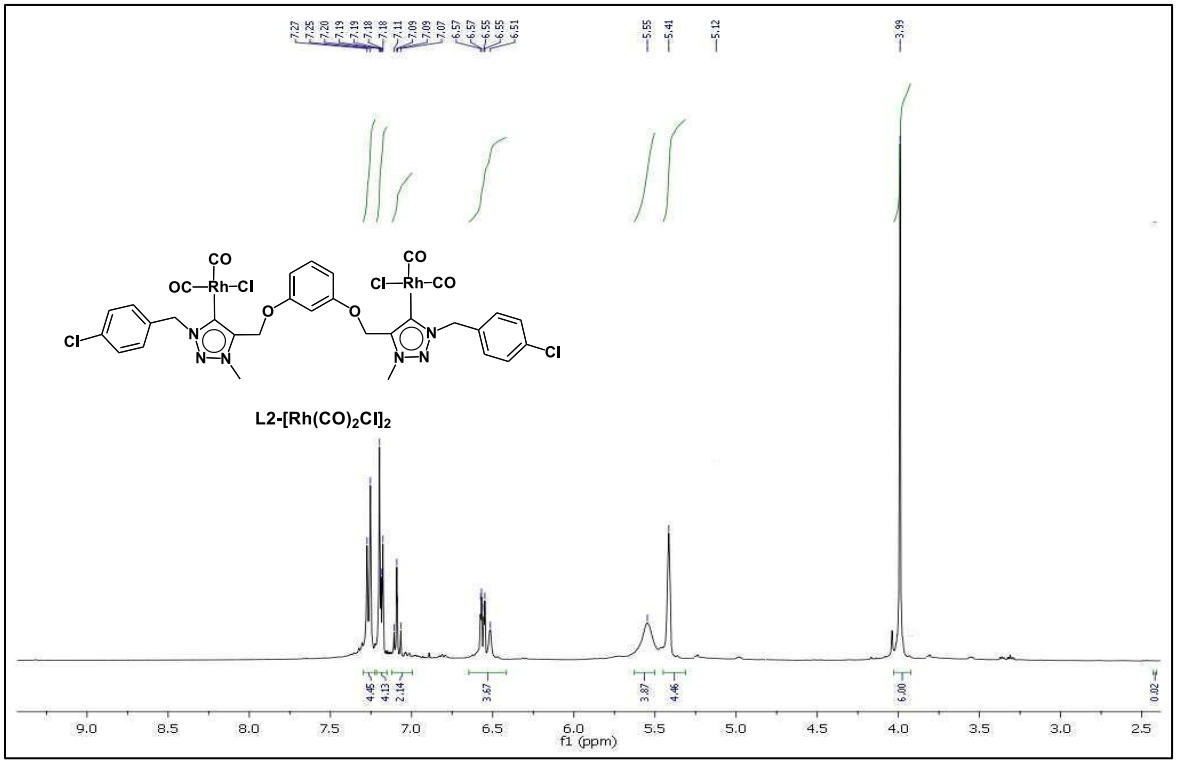

Figure S35. ^{1}H NMR (400 MHz) spectrum for **L2**-$[Rh(CO)_2Cl]_2$ in $CDCl_3$

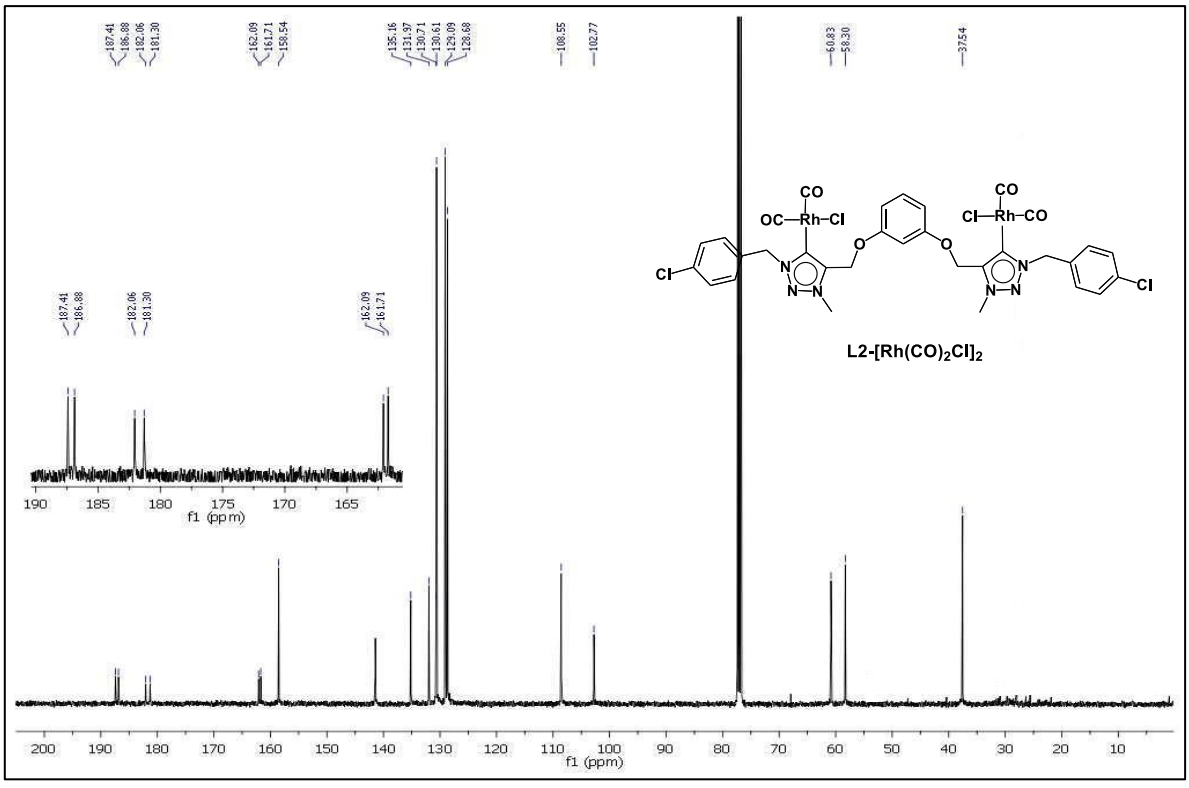

Figure S36. ^{13}C NMR (100 MHz) spectrum for **L2**-$[Rh(CO)_2Cl]_2$ in $CDCl_3$

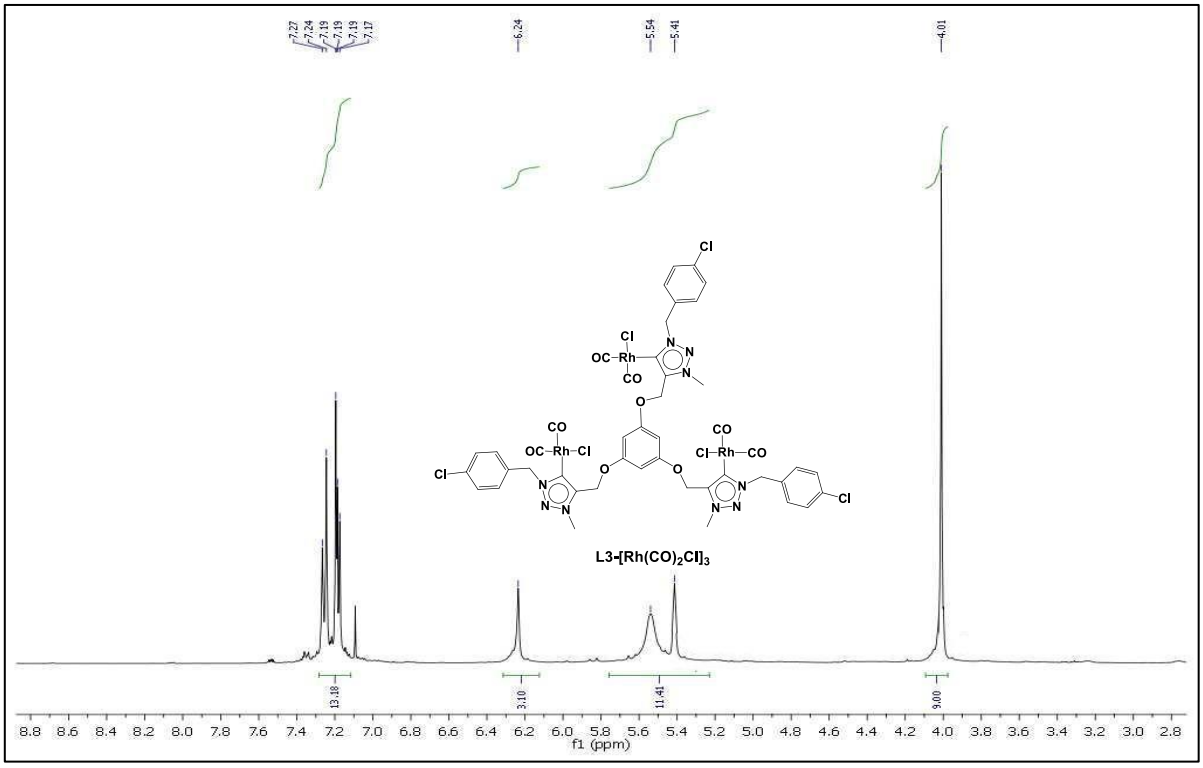

Figure S37. ^{1}H NMR (400 MHz) spectrum for **L3**-$[Rh(CO)_2Cl]_3$ in $CDCl_3$

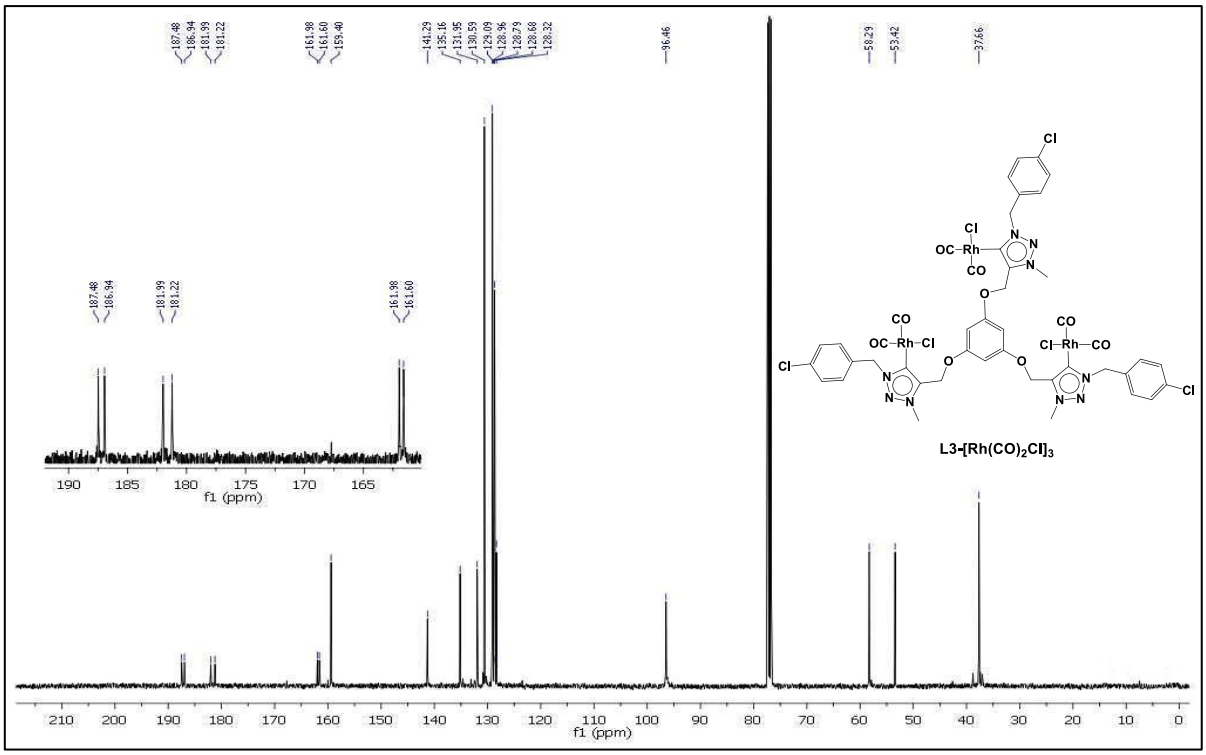

Figure S38. ^{13}C NMR (100 MHz) spectrum for **L3**-$[Rh(CO)_2Cl]_3$ in $CDCl_3$

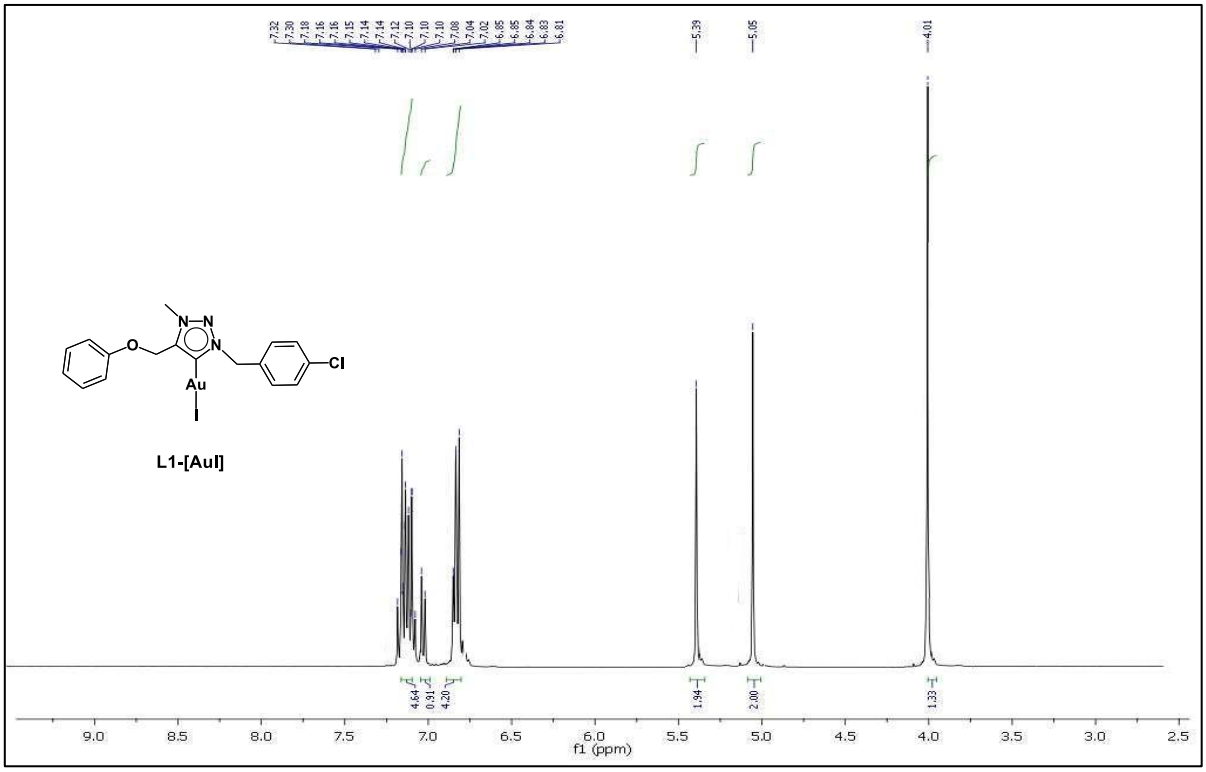

Figure S39. ^{1}H NMR (400 MHz) spectrum for **L1**-[AuI] in $CDCl_3$

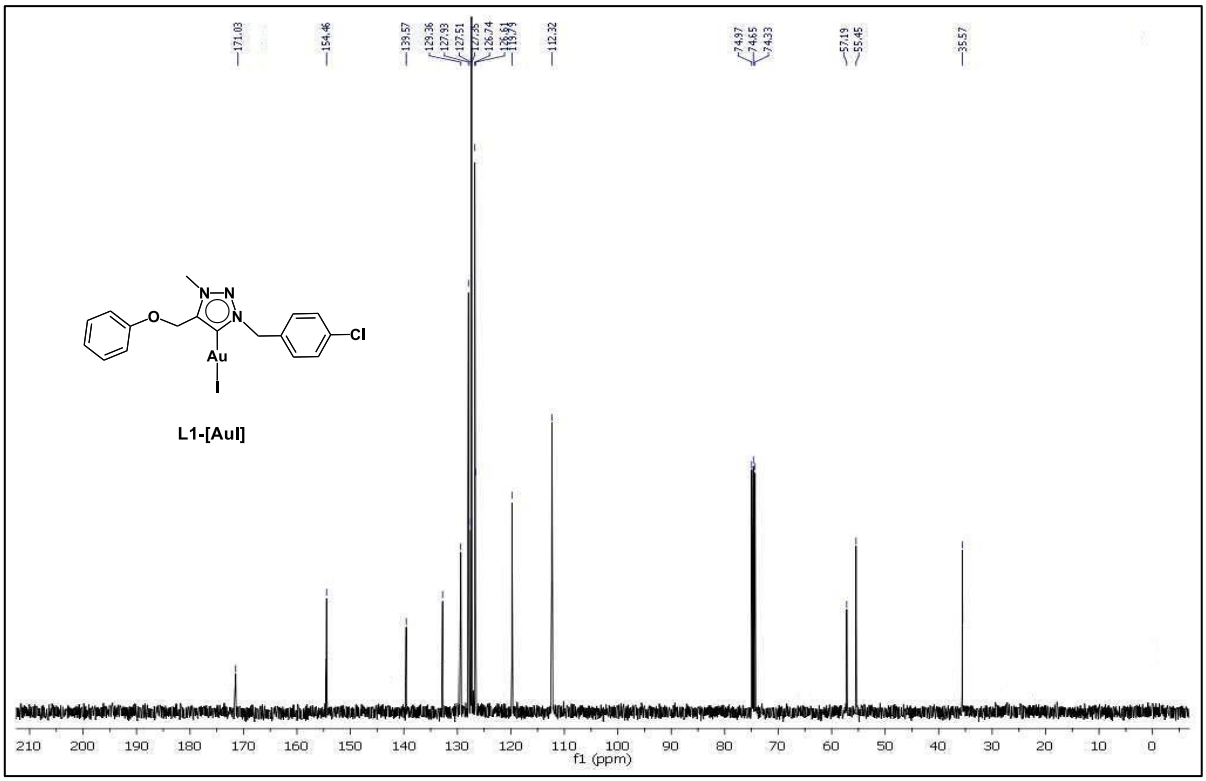

Figure S40. ^{13}C NMR (100 MHz) spectrum for **L1**-[AuI] in $CDCl_3$

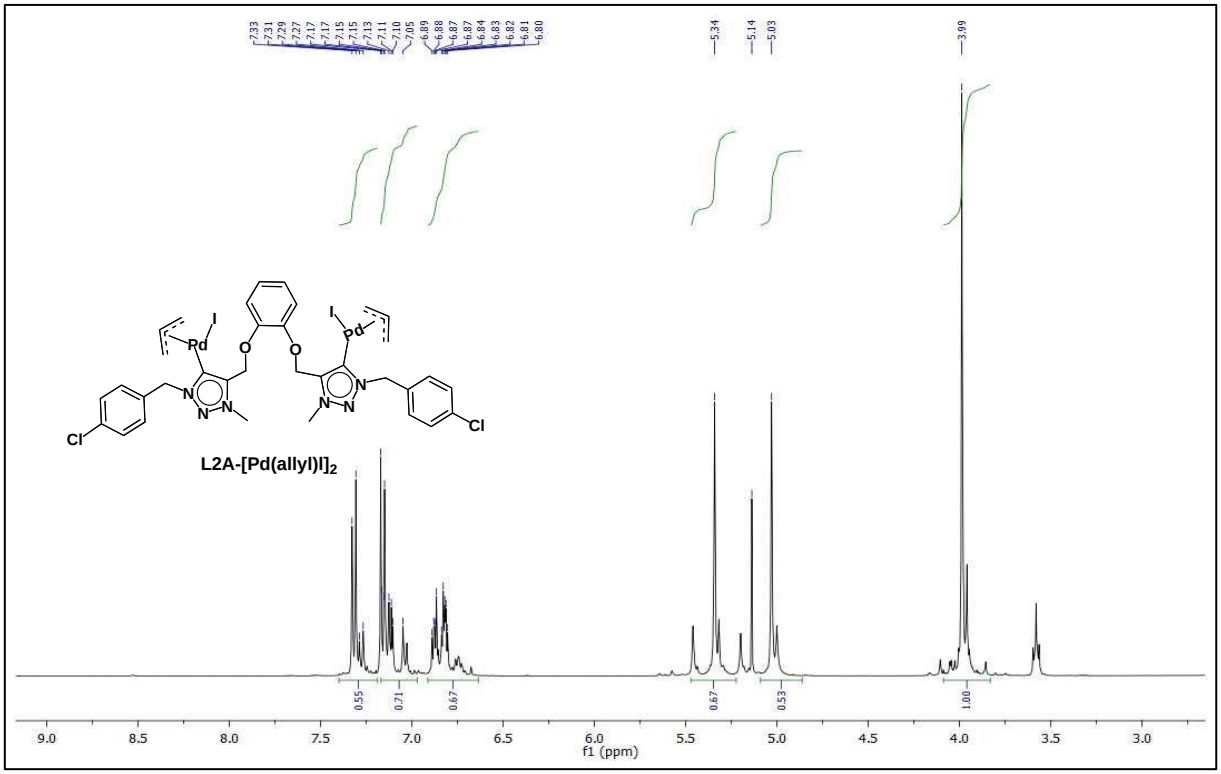

Figure S41. ^{1}H NMR (400 MHz) spectrum for **L2A**-[Pd(allyl)I]$_2$ in $CDCl_3$

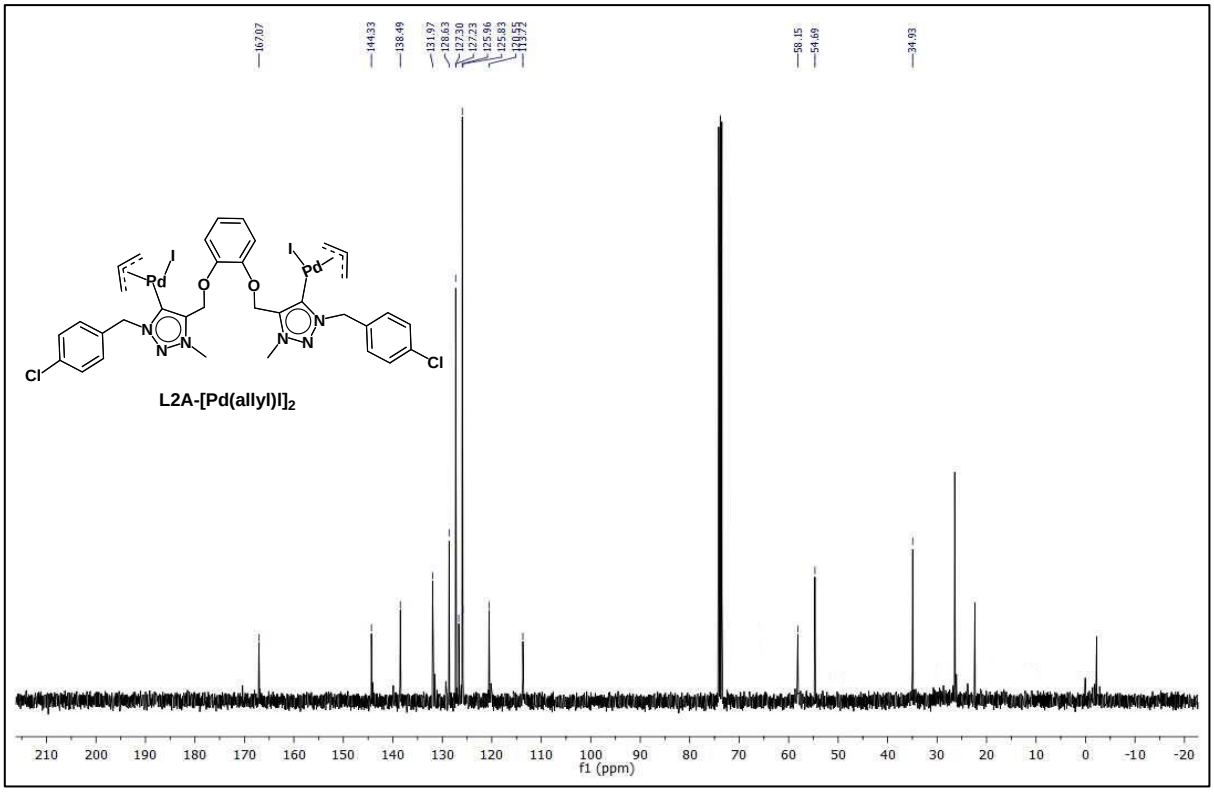

Figure S42. ^{13}C NMR (100 MHz) spectrum for **L2A**-[Pd(allyl)I]$_2$ in $CDCl_3$

^{1}H (400 MHz) and ^{13}C NMR (100 MHz) Spectra for products of α-arylation in $CDCl_3$

Figure S43. ^{1}H NMR (400 MHz) spectrum for product Table 1, entry 3

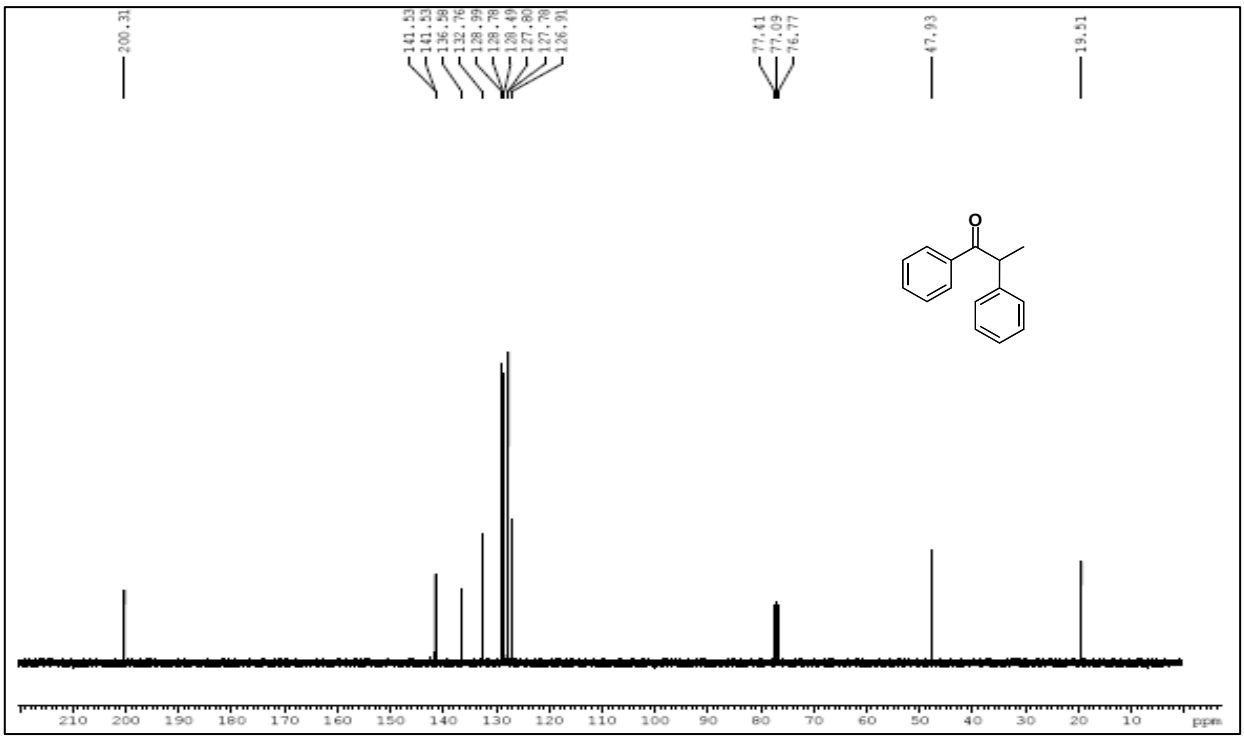

Figure S44. ^{13}C NMR (100 MHz) spectrum product Table 1, entry 3

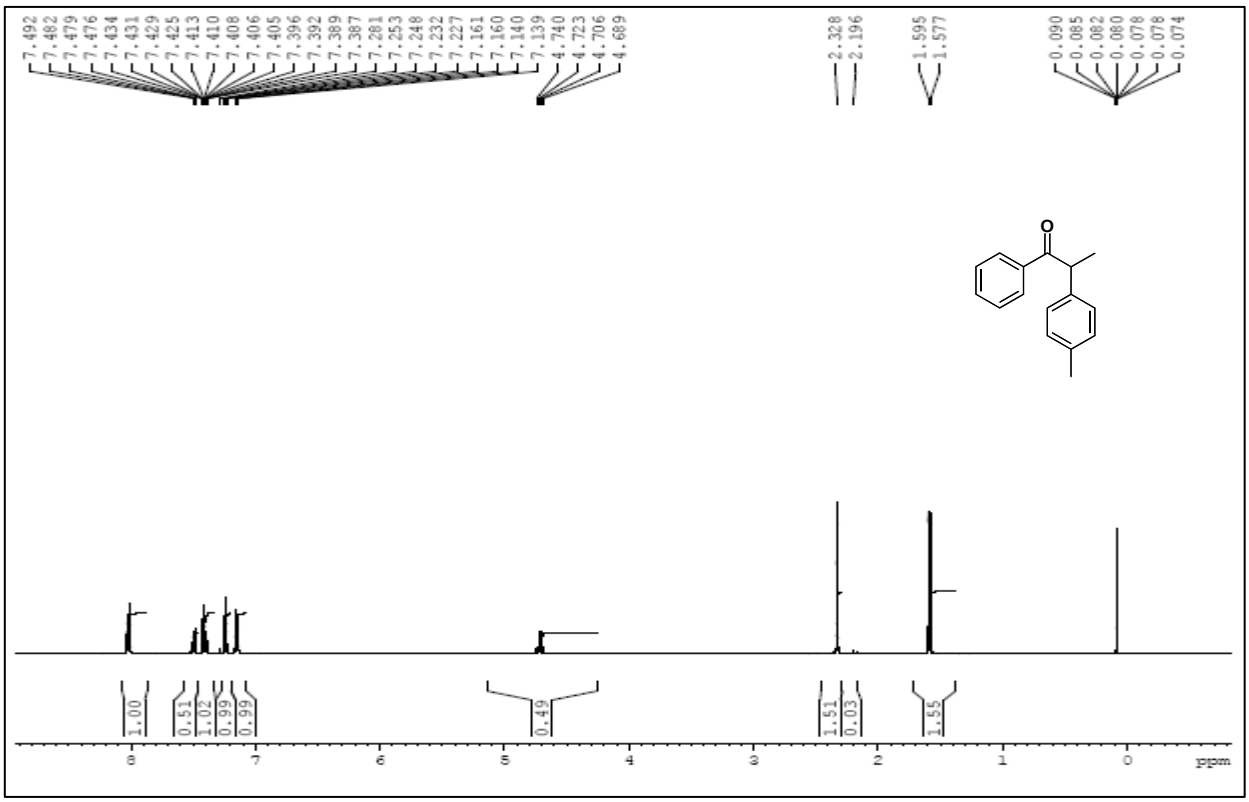

Figure S45. [1]H NMR (400 MHz) spectrum for product Table 1, entry 6

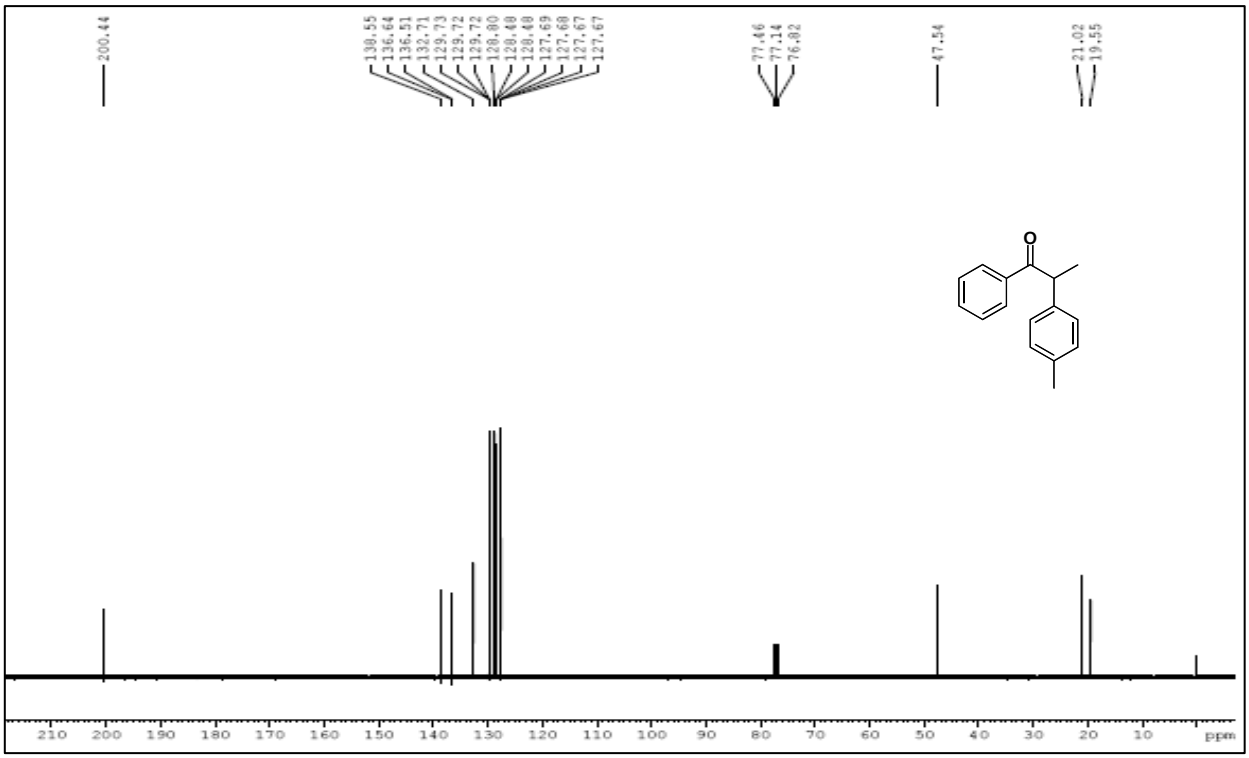

Figure S46. [13]C NMR (100 MHz) spectrum product Table 1, entry 6

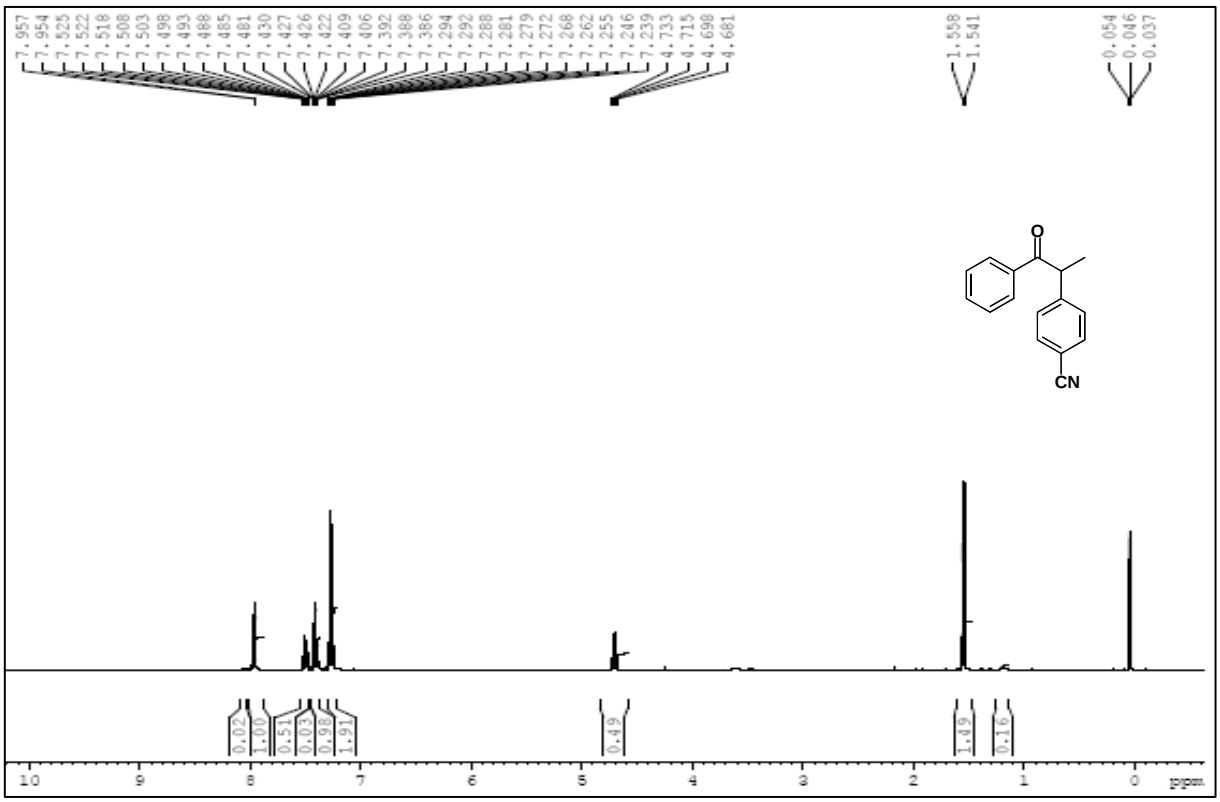

Figure S47. ^{1}H NMR (400 MHz) spectrum for product Table 1, entry 9

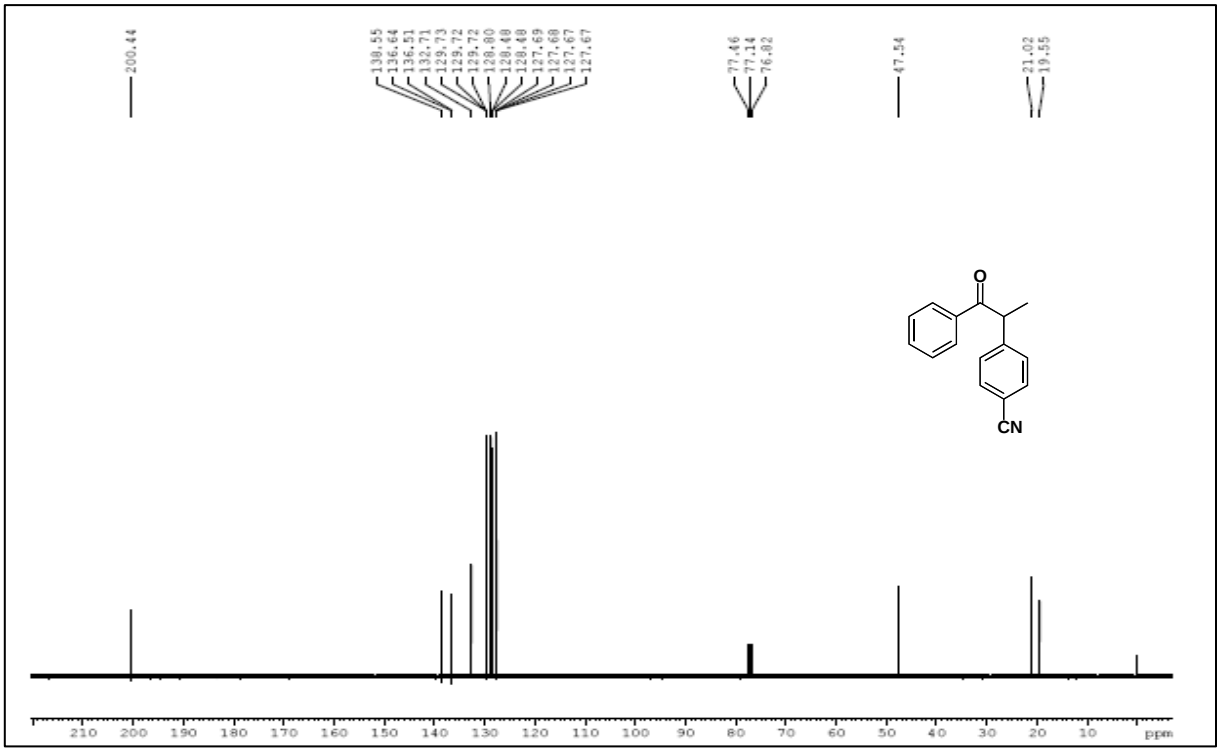

Figure S48. ^{13}C NMR (100 MHz) spectrum product Table 1, entry 9

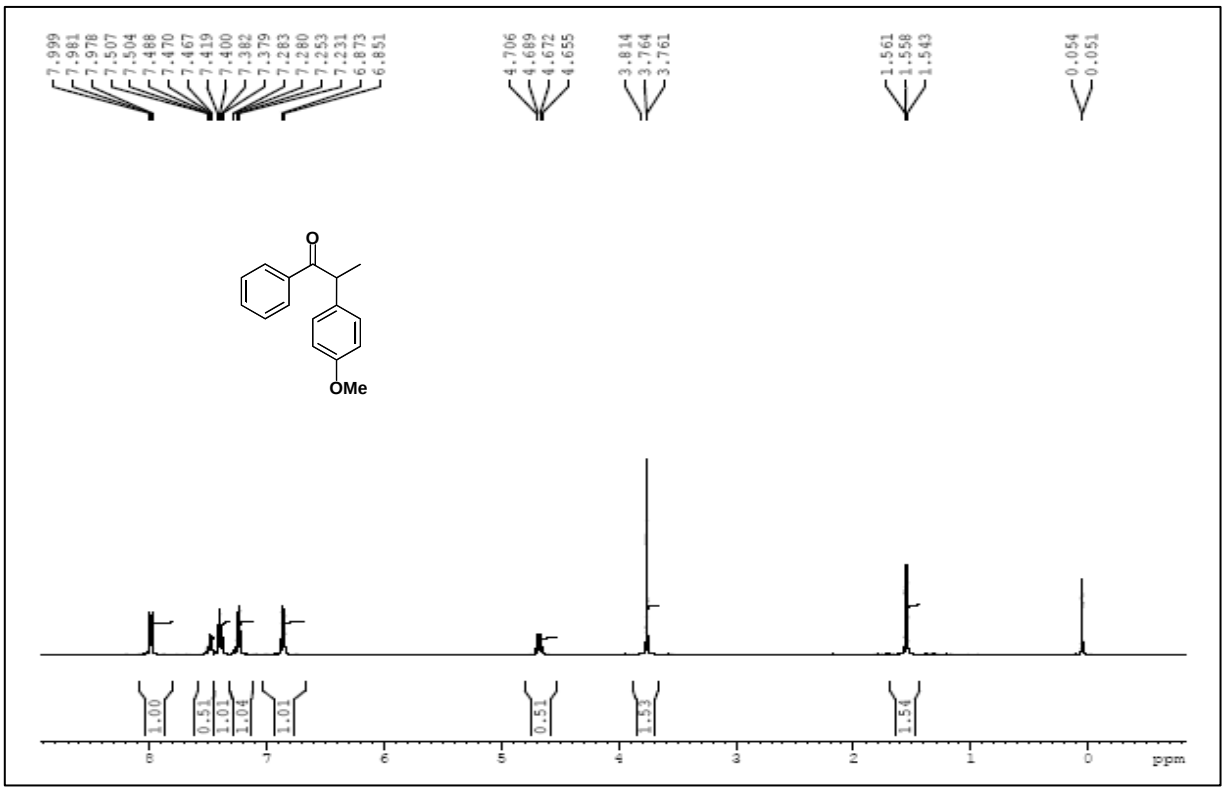

Figure S49. ^{1}H NMR (400 MHz) spectrum for product Table 1, entry 12

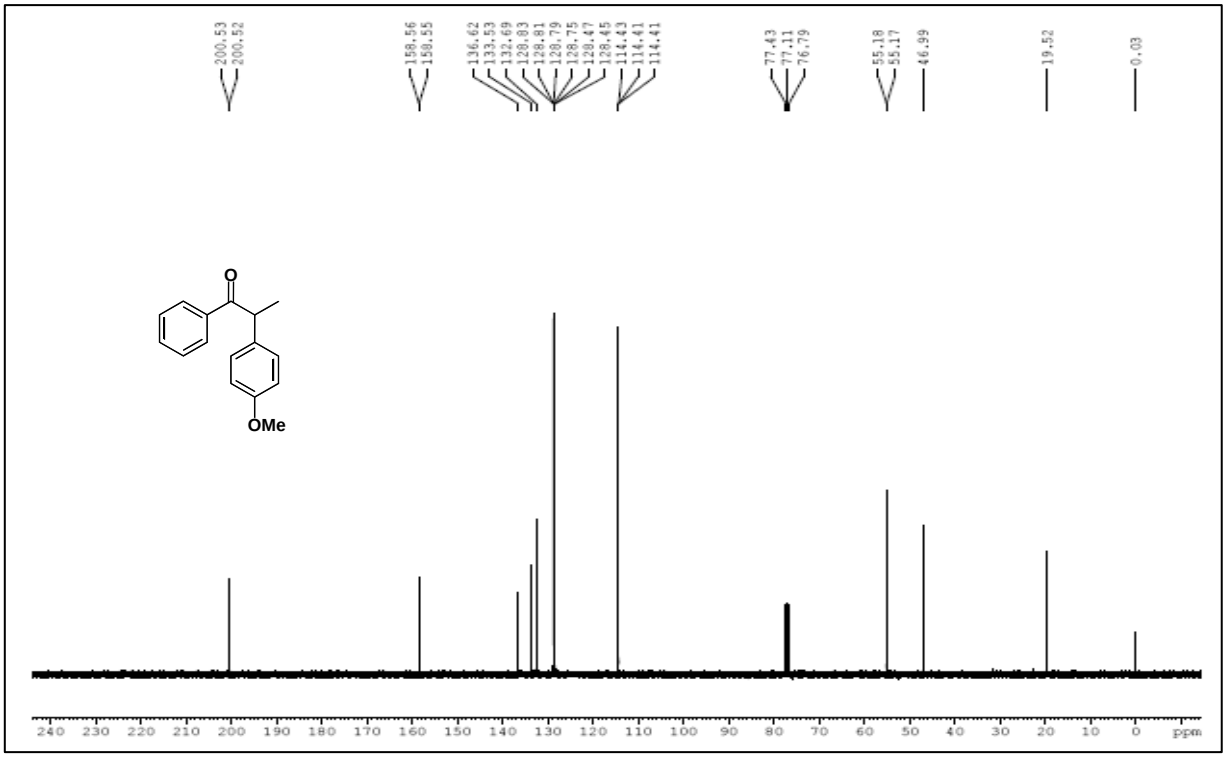

Figure S50. ^{13}C NMR (100 MHz) spectrum product Table 1, entry 12

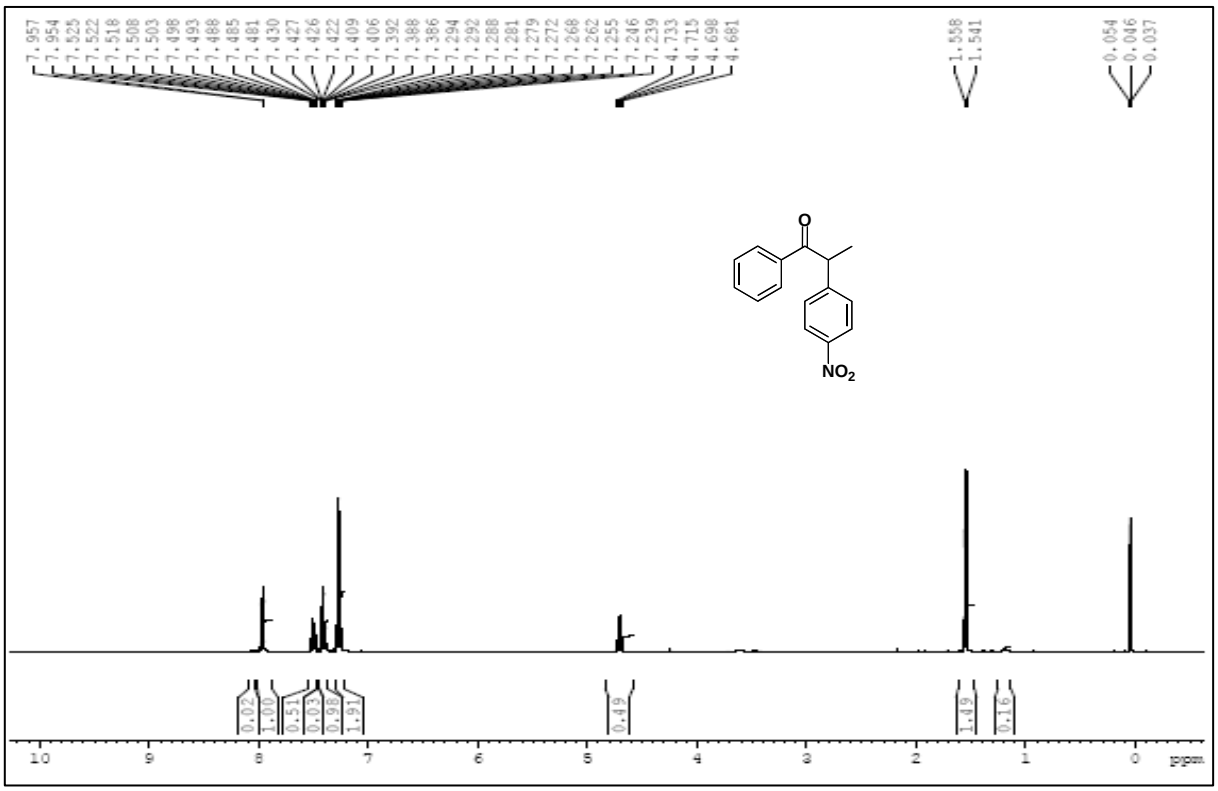

Figure S51. ^{1}H NMR (400 MHz) spectrum for product Table 1, entry 14

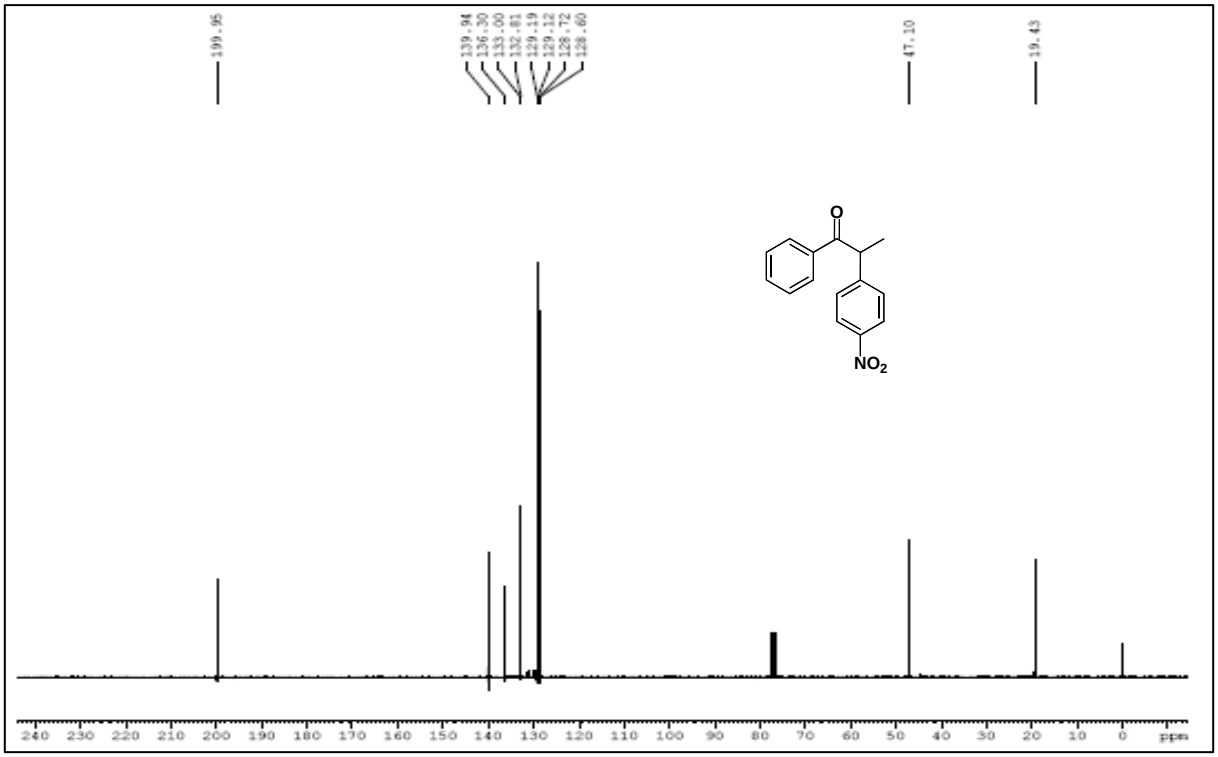

Figure S52. ^{13}C NMR (100 MHz) spectrum product Table 1, entry 15

^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) Spectra for products of Suzuki-Miyaura in $CDCl_3$

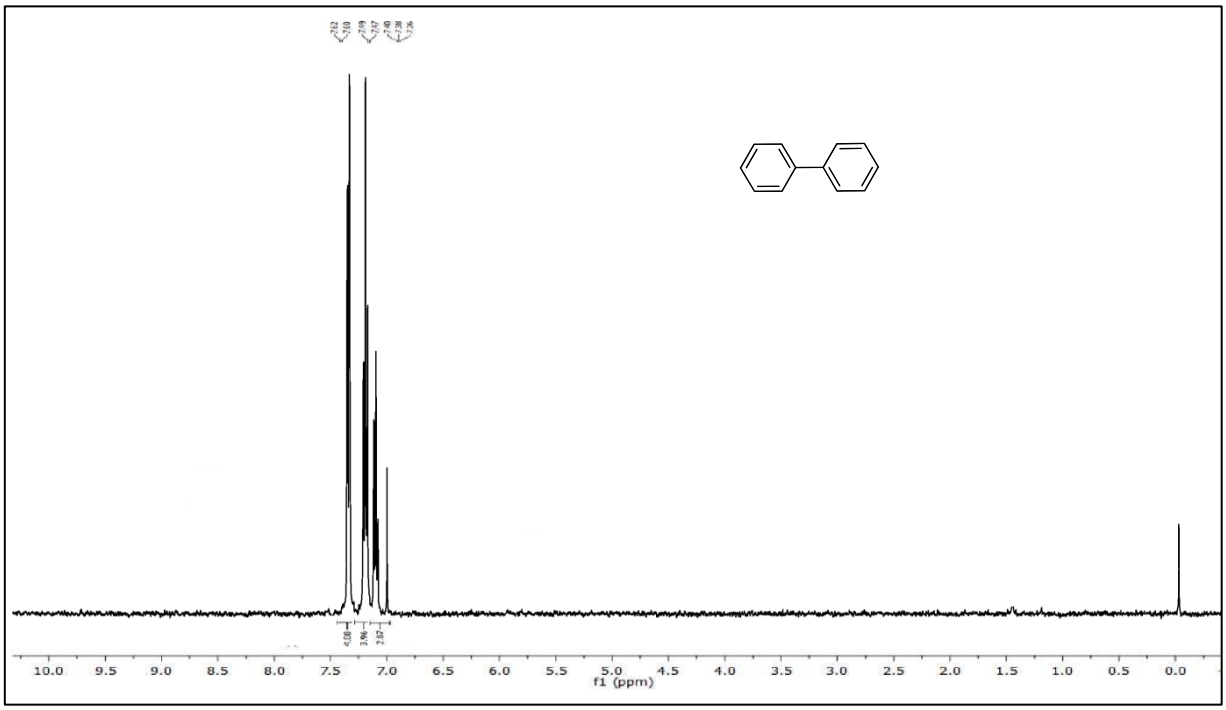

Figure S53. ^{1}H NMR (400 MHz) spectrum for product Table 2, entry 4

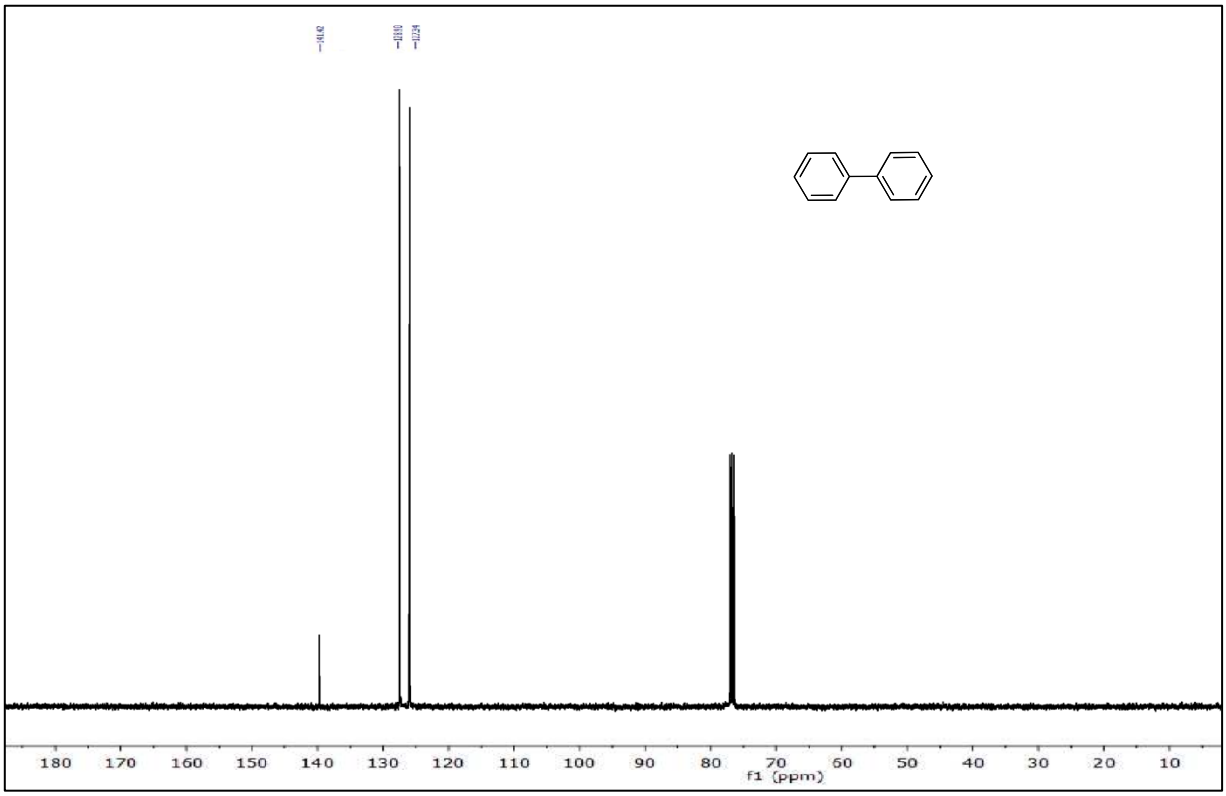

Figure S54. ^{13}C NMR (100 MHz) spectrum product Table 2, entry 4

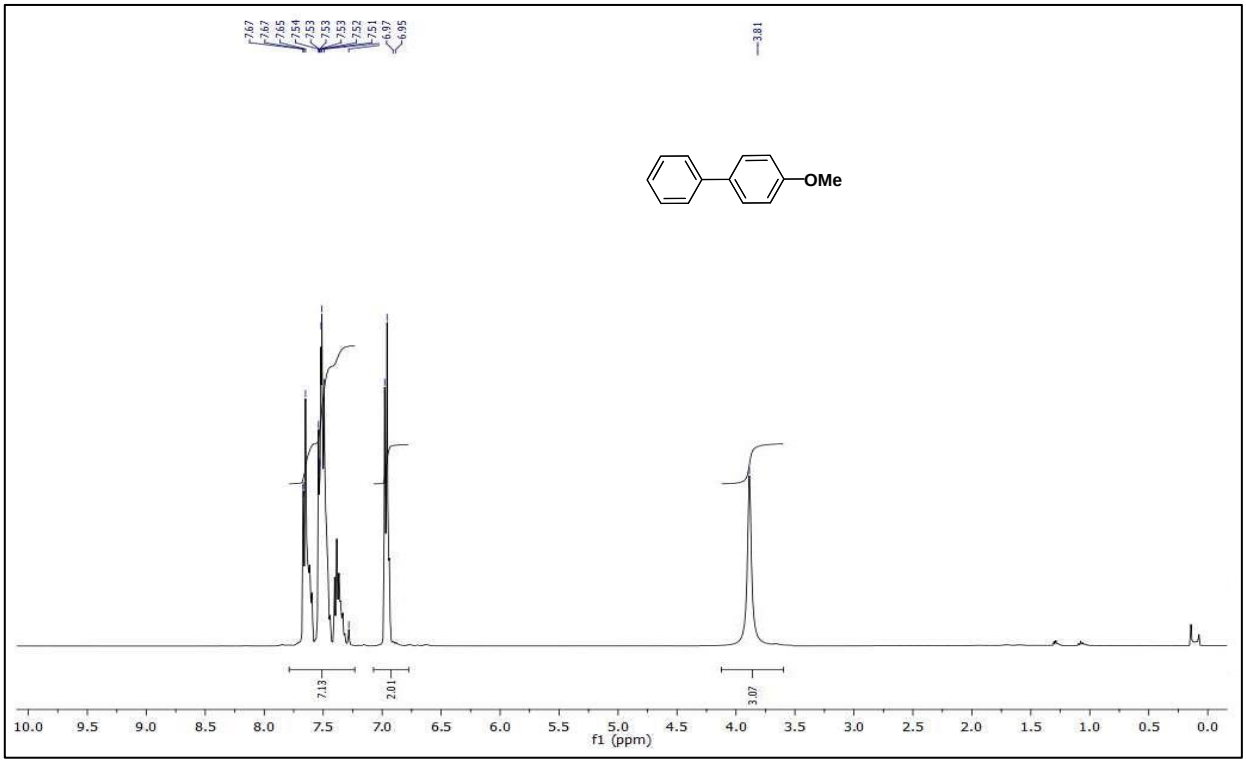

Figure S55. ^{1}H NMR (400 MHz) spectrum for product Table 2, entry 8

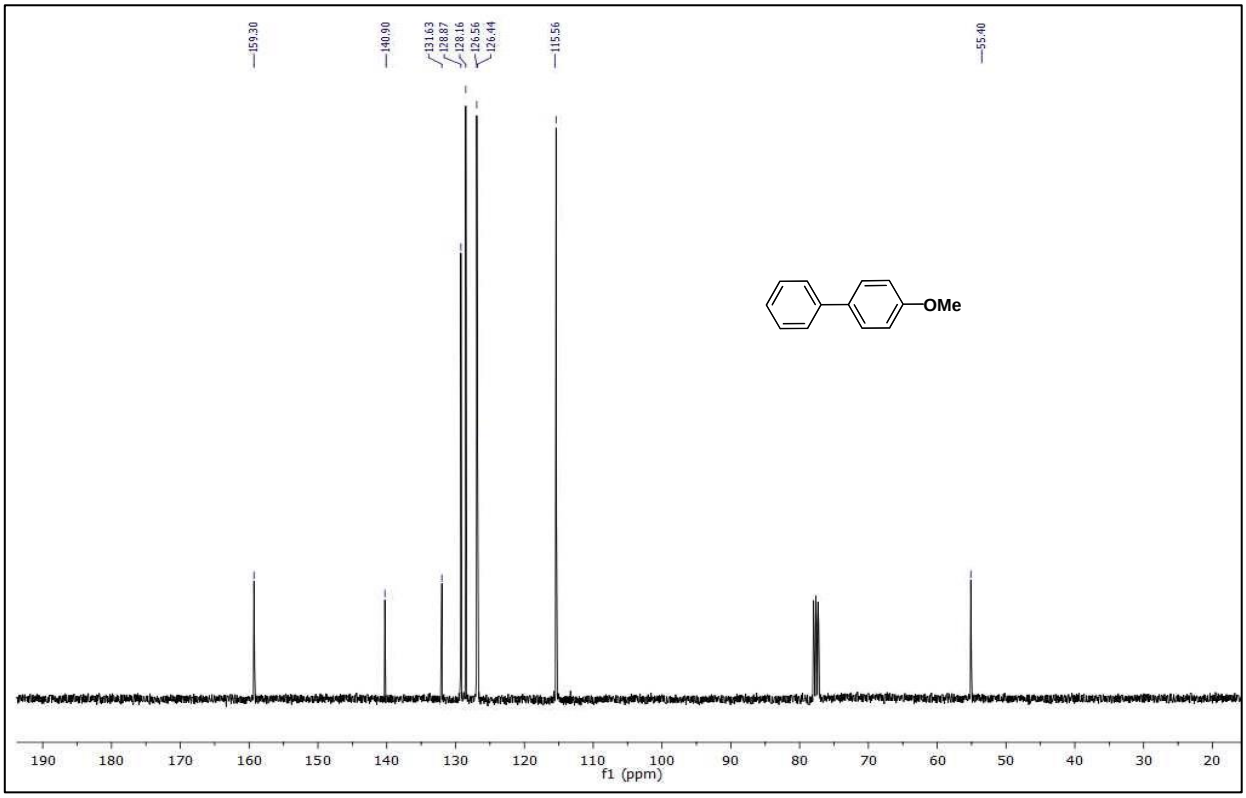

Figure S56. ^{13}C NMR (100 MHz) spectrum product Table 2, entry 8

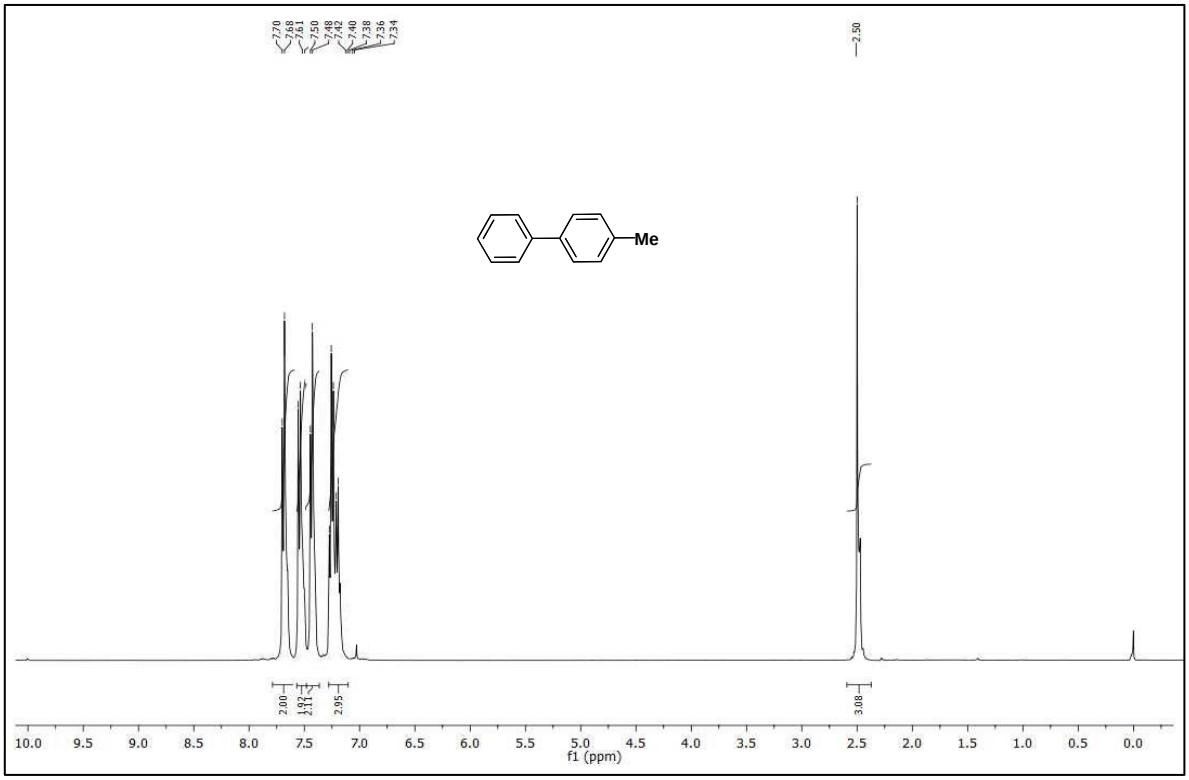

Figure S57. ^{1}H NMR (400 MHz) spectrum for product Table 2, entry 12

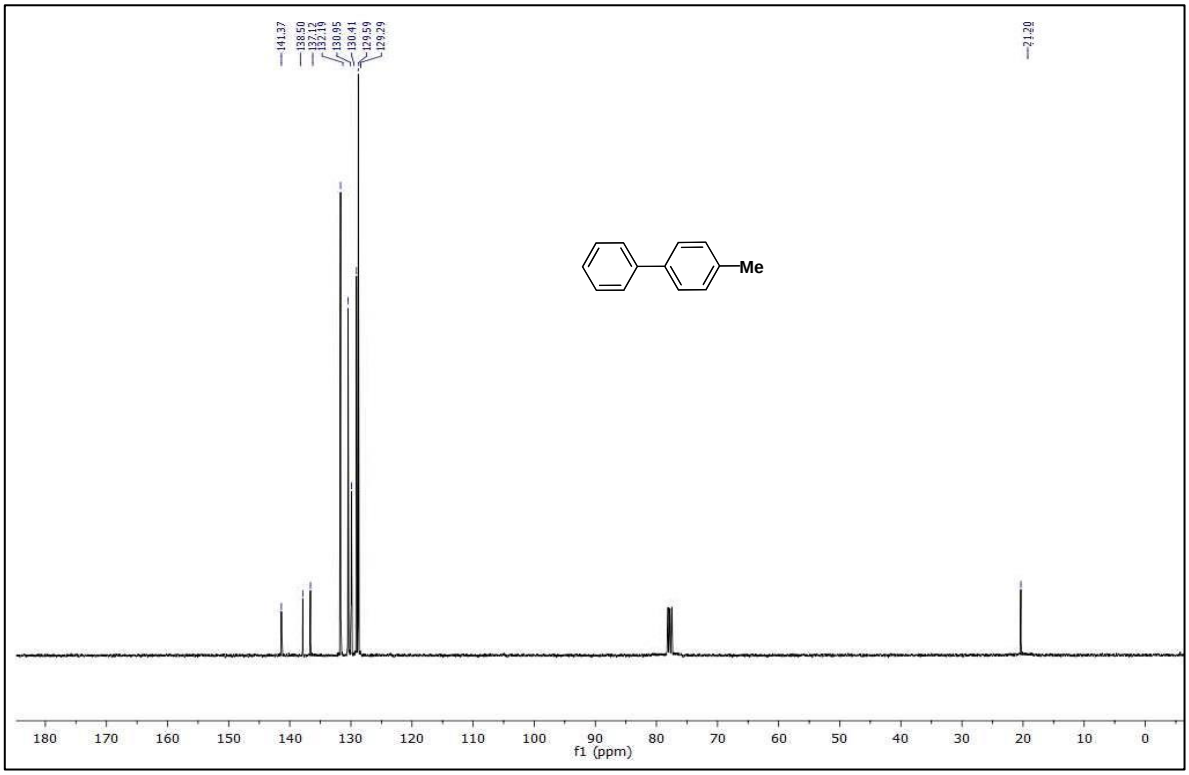

Figure S58. ^{13}C NMR (100 MHz) spectrum product Table 2, entry 12

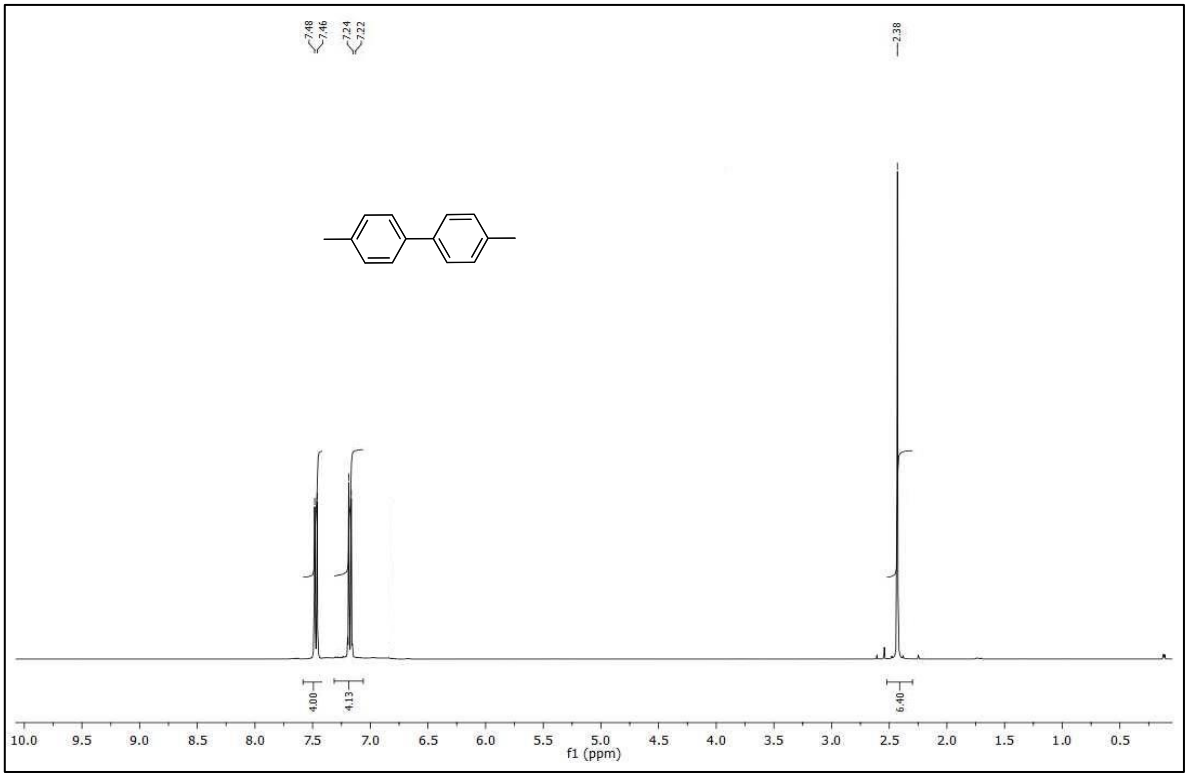

Figure S59. ^{1}H NMR (400 MHz) spectrum for product Table 2, entry 15

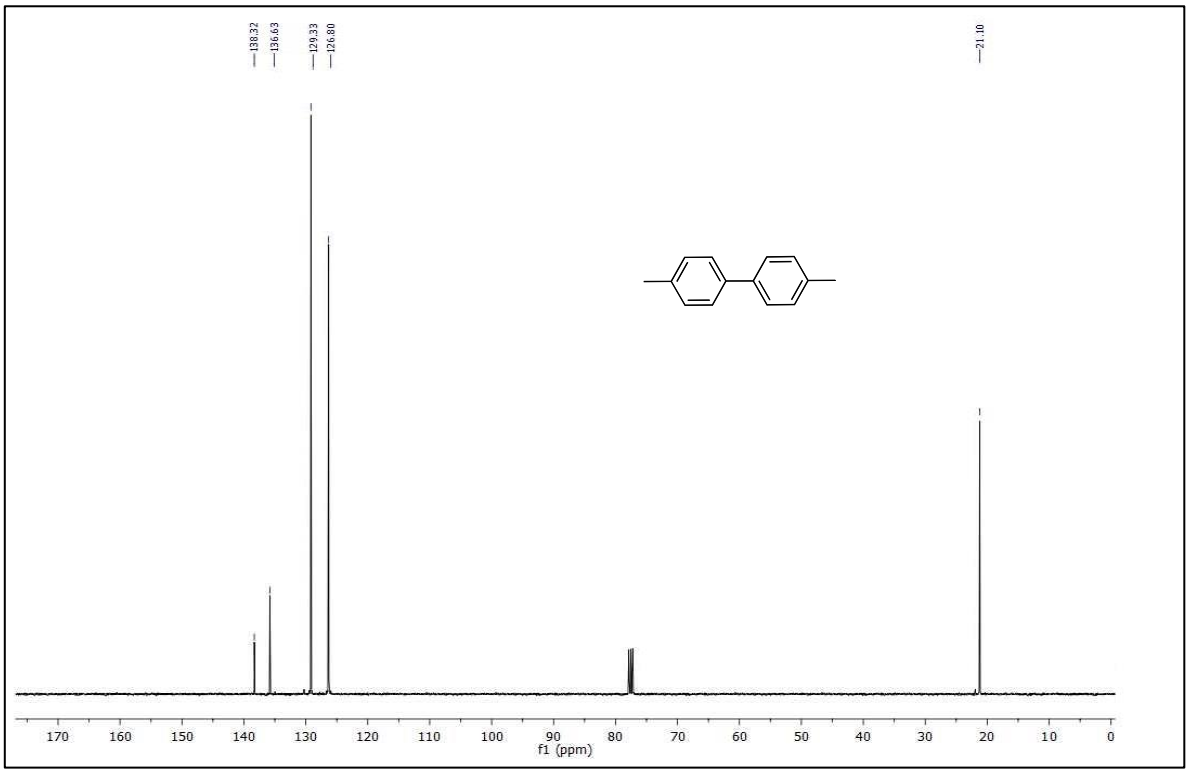

Figure S60. ^{13}C NMR (100 MHz) spectrum product Table 2, entry 15

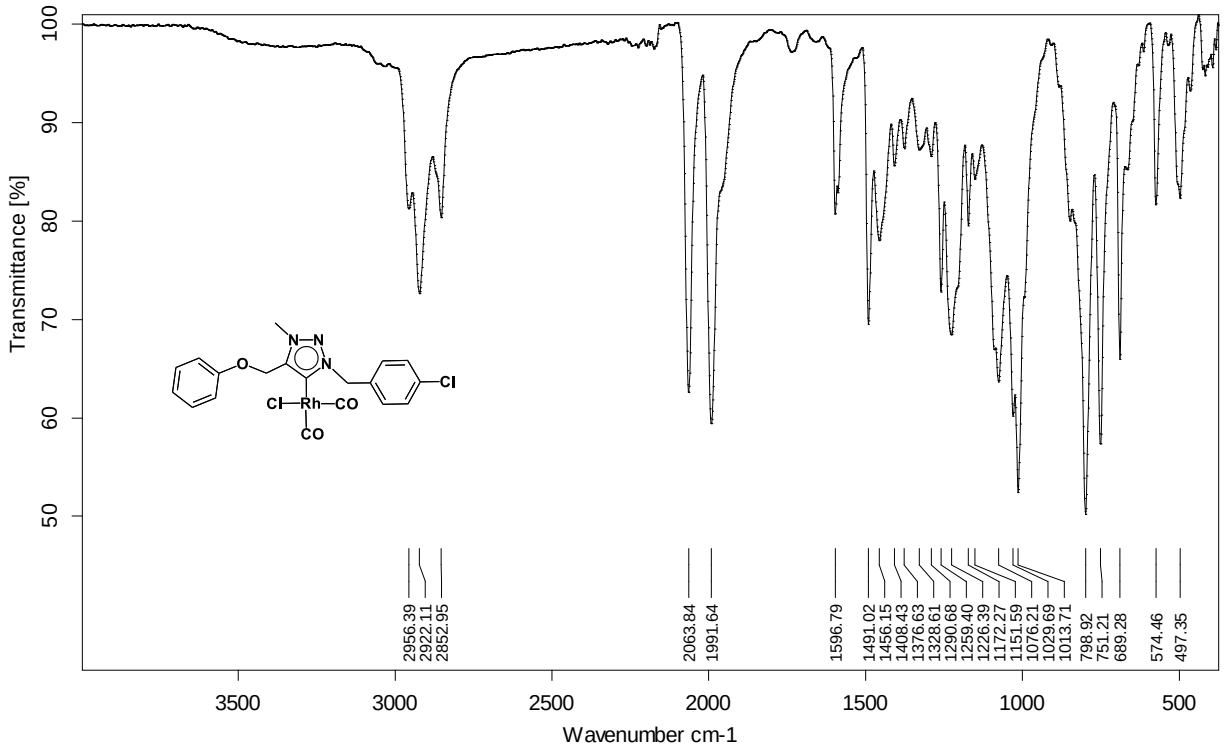

Figure S61. FT-IR Spectra for **L1**-[$Rh(CO)_2Cl$]

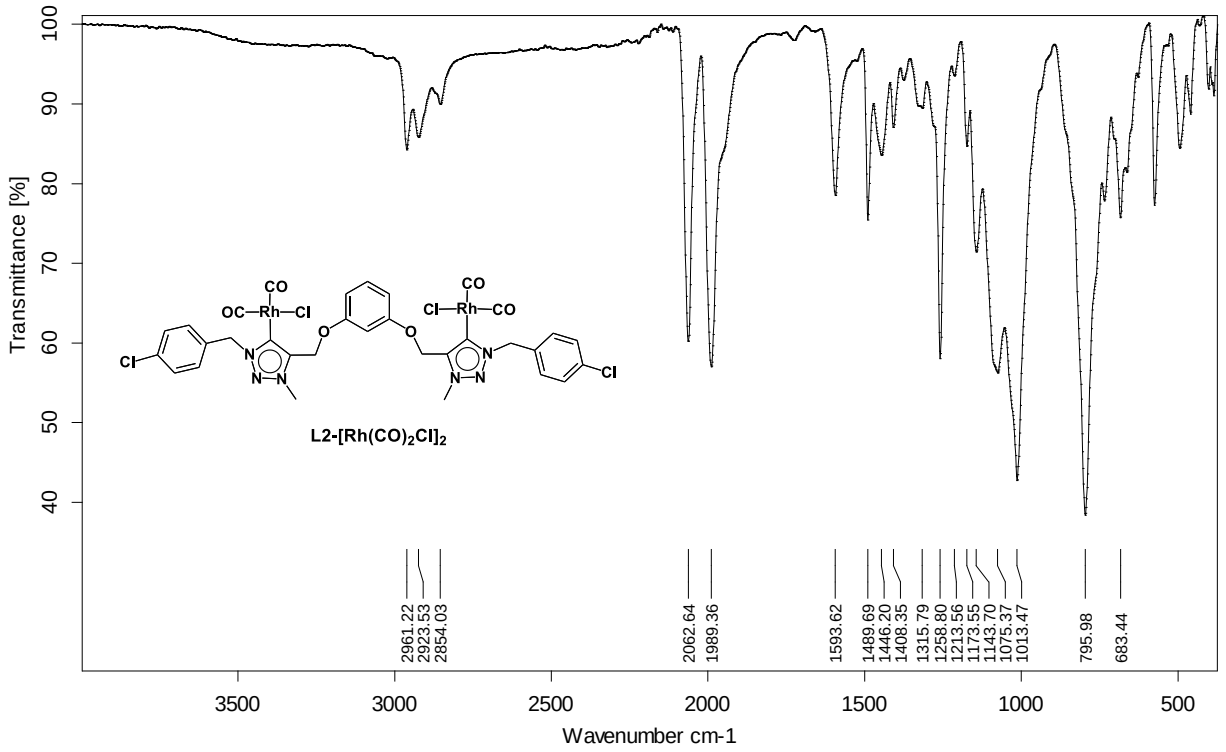

Figure S62. FT-IR Spectra for **L2**-[$Rh(CO)_2Cl]_2$

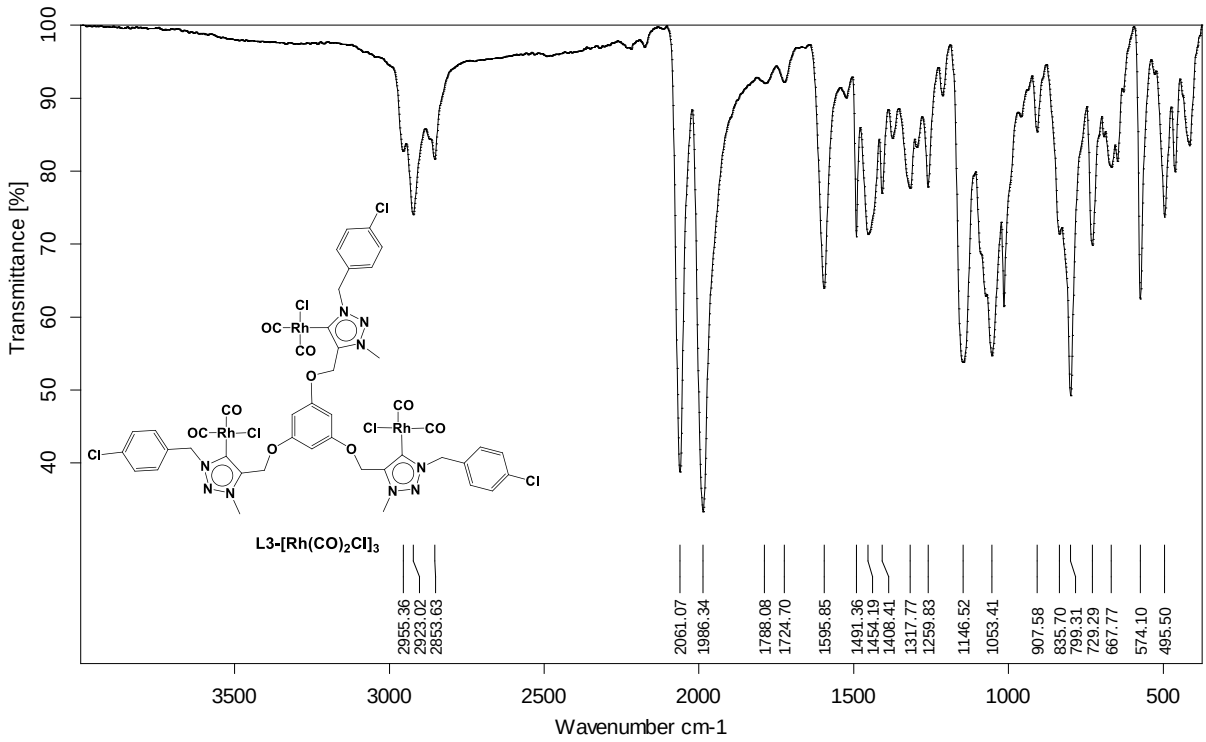

Figure S63. FT-IR Spectra for **L3**-$[Rh(CO)_2Cl]_3$

Conversion results for catalytic poisoning with elemental Hg and DCT

Methoxycyclization of enyne E1

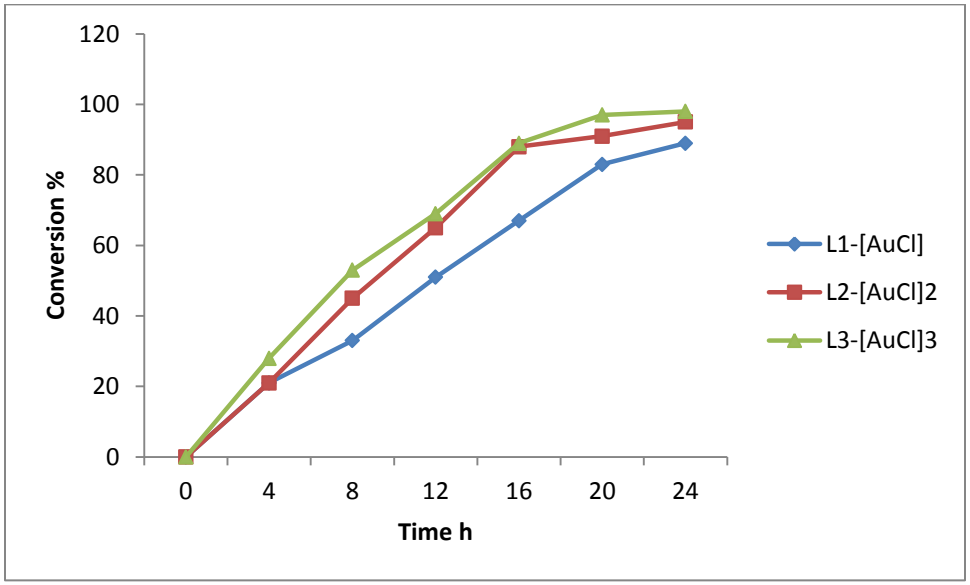

Figure S64. Catalytic performance of multinuclear gold complexes **Ln**-[AuCl]n in the synthesis of enyne **E1**

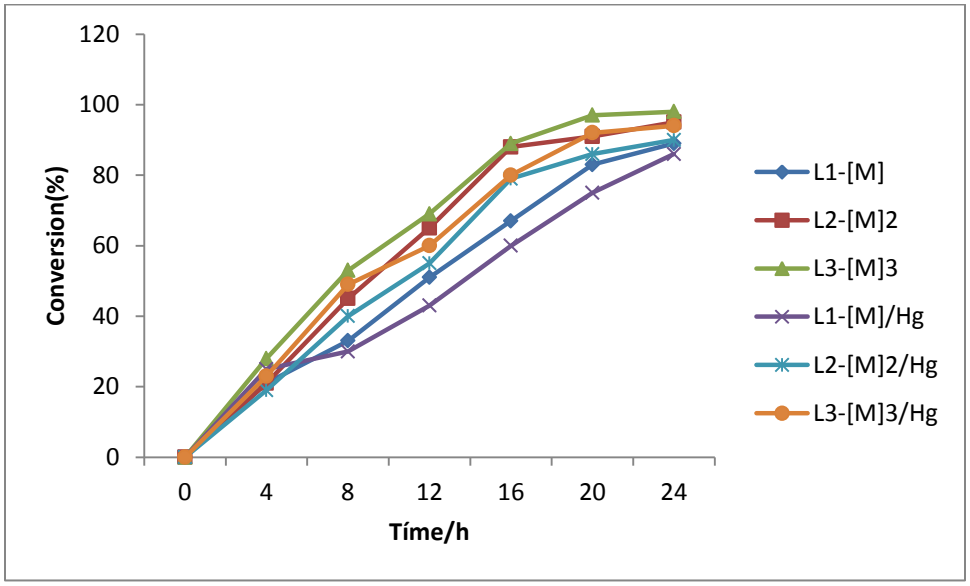

Figure S65. Reaction inhibition of enyne **E1** formation with the addition of elemental Hg using catalysts **Ln**-[AuCl]n (n = 1-3)

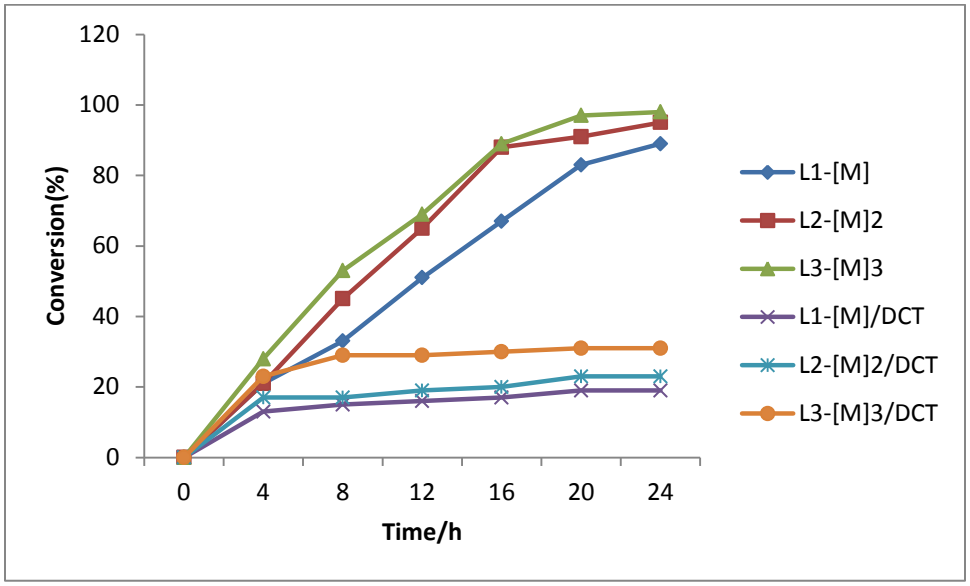

Figure S66. Reaction inhibition of enyne **E1** formation with the addition of DCT (t = 0) using catalysts **Ln**-[AuCl]n

Alpha arylation of propiophenone

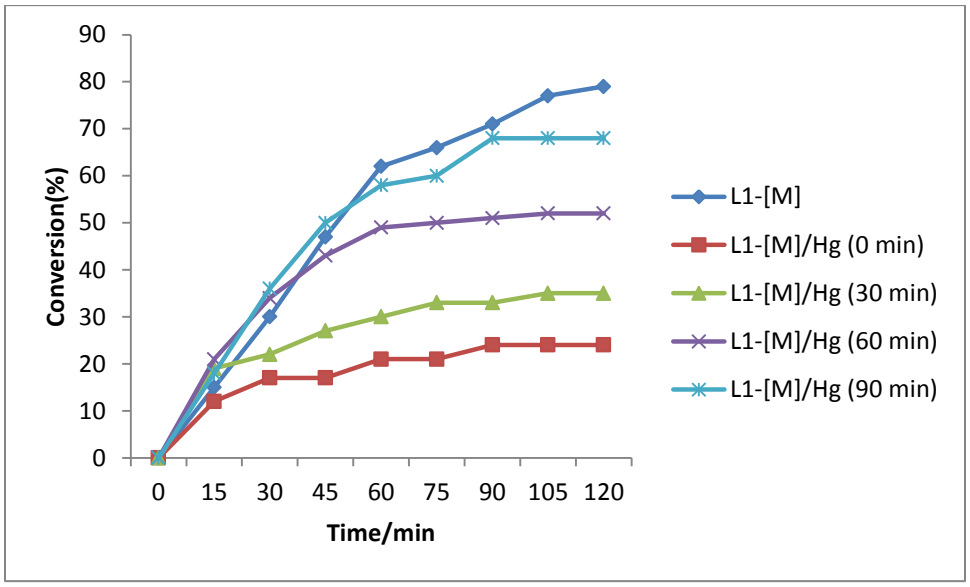

Figure S67. Reaction inhibition of 1-phenyl-2-(phenyl)-1-propanone formation with the addition of elemental Hg using catalyst **L1**-[Pd(allyl)Cl]

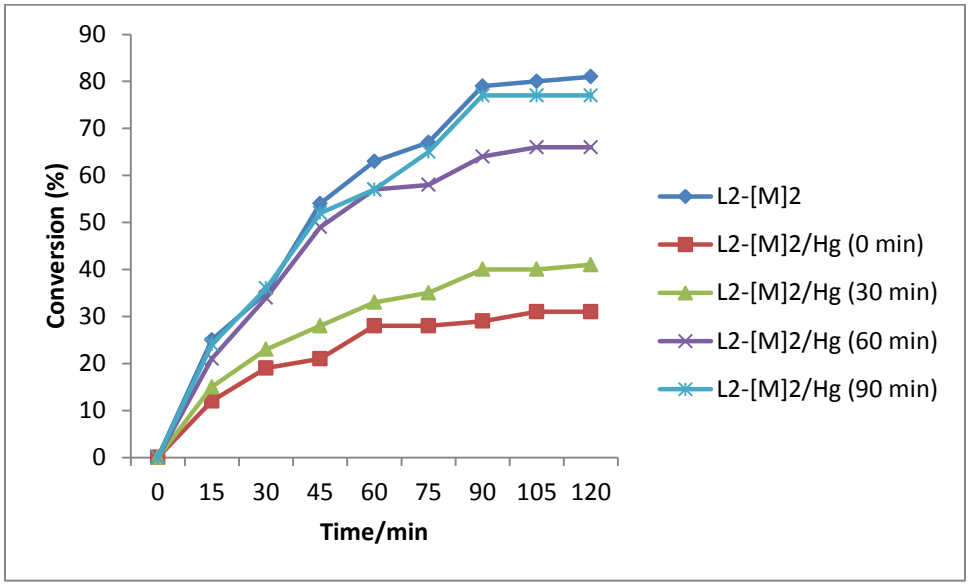

Figure S68. Reaction inhibition of 1-phenyl-2-(phenyl)-1-propanone formation with the addition of elemental Hg using catalyst **L2**-$[Pd(allyl)Cl]_2$

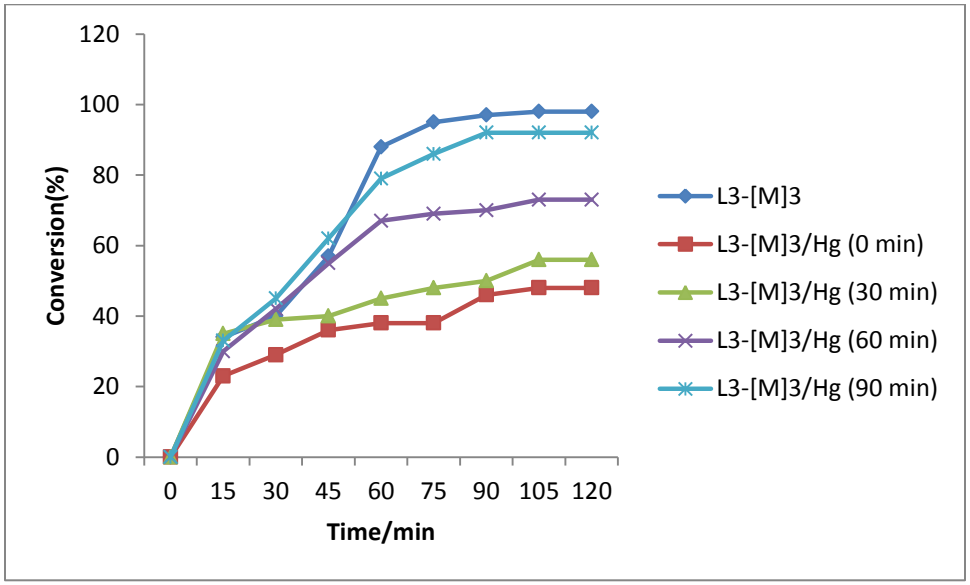

Figure S69. Reaction inhibition of 1-phenyl-2-(phenyl)-1-propanone formation with the addition of elemental Hg using catalyst **L3**-$[Pd(allyl)Cl]_3$

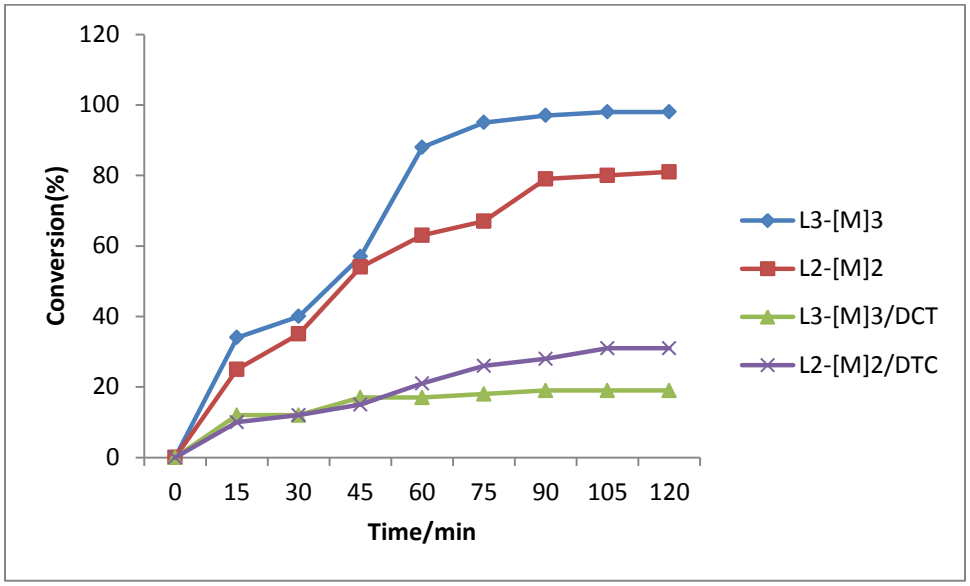

Figure S70. Reaction inhibition of 1-phenyl-2-(phenyl)-1-propanone formation with the addition of DCT (t = 0) using catalysts **Ln**-[Pd(allyl)Cl]n (n = 2-3)

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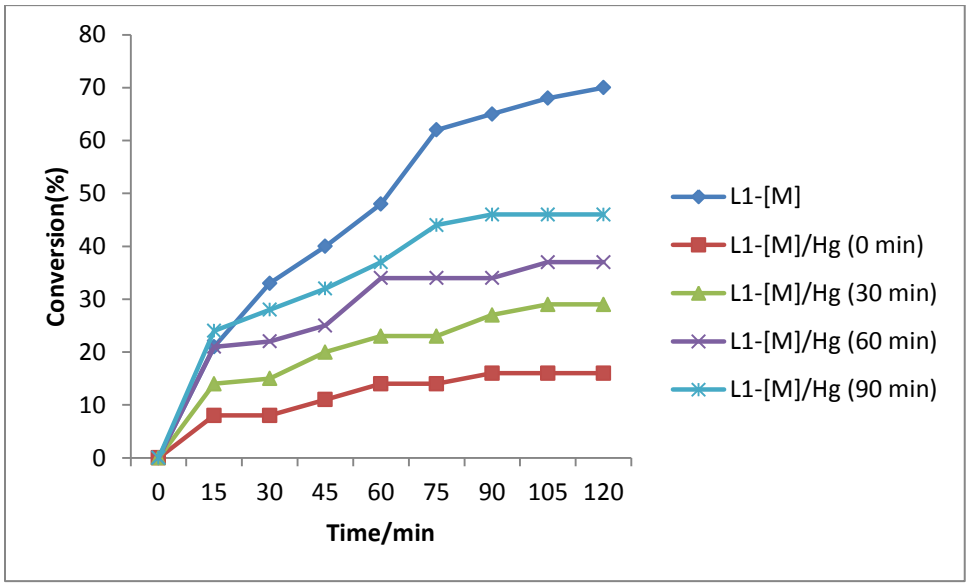

Figure S71. Reaction inhibition of biphenyl formation with the addition of elemental mercury at different times using catalyst **L1**-[Pd(allyl)Cl]

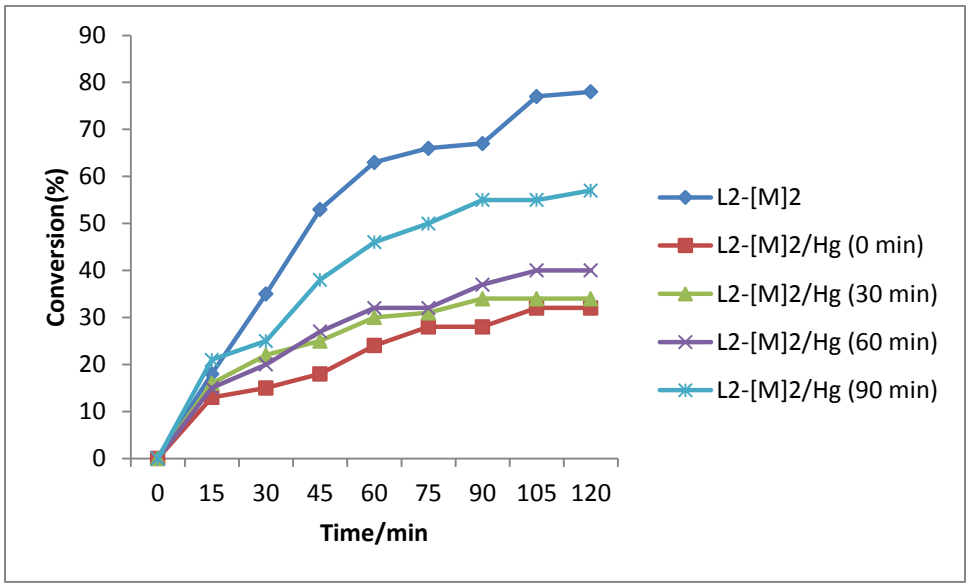

Figure S72. Reaction inhibition of biphenyl formation with the addition of elemental mercury at different times using catalyst **L2**-[Pd(allyl)Cl]$_2$

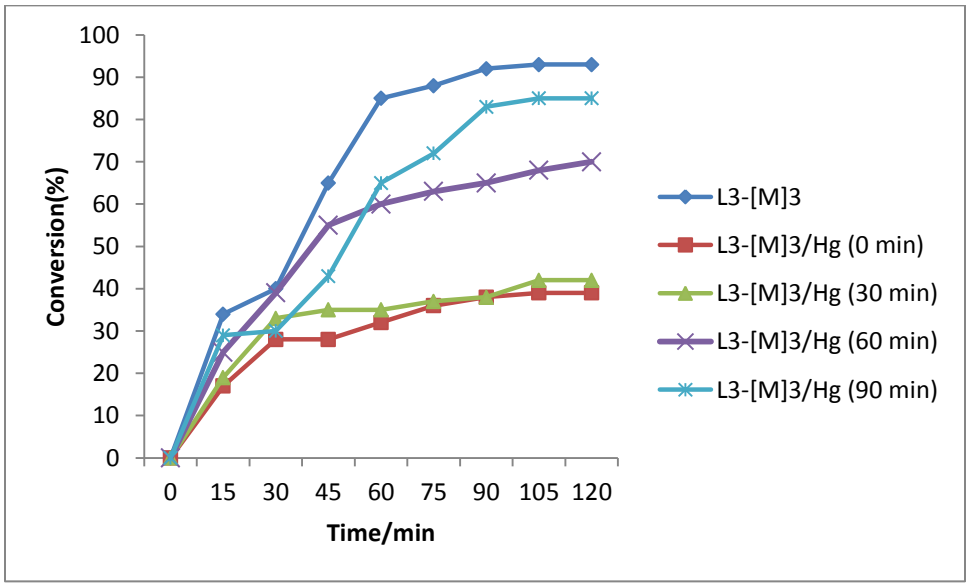

Figure S73. Reaction inhibition of biphenyl formation with the addition of elemental mercury at different times using catalyst **L3**-[Pd(allyl)Cl]$_3$

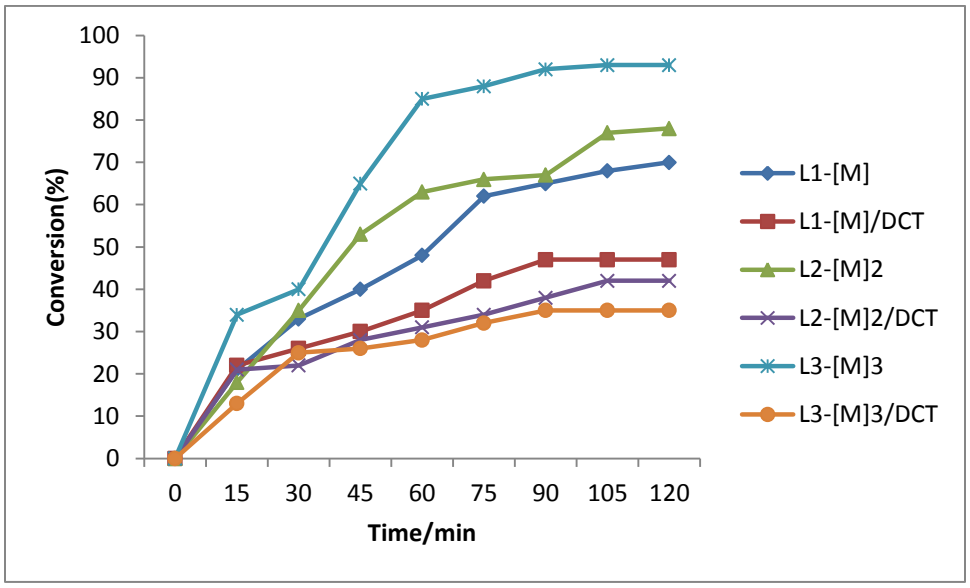

Figure S74. Reaction inhibition of biphenyl formation with the addition of DCT (t = 0) using catalysts **Ln**-[Pd(allyl)Cl]$_n$

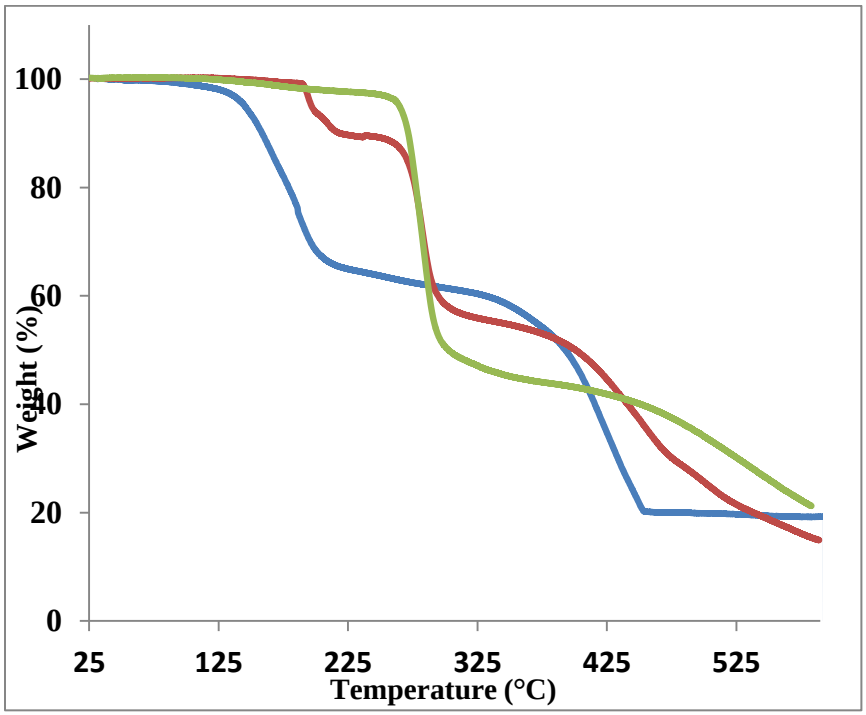

Figure S75. TGA graphic and data for precatalysts **Ln**-[Pd(allyl)Cl]$_n$

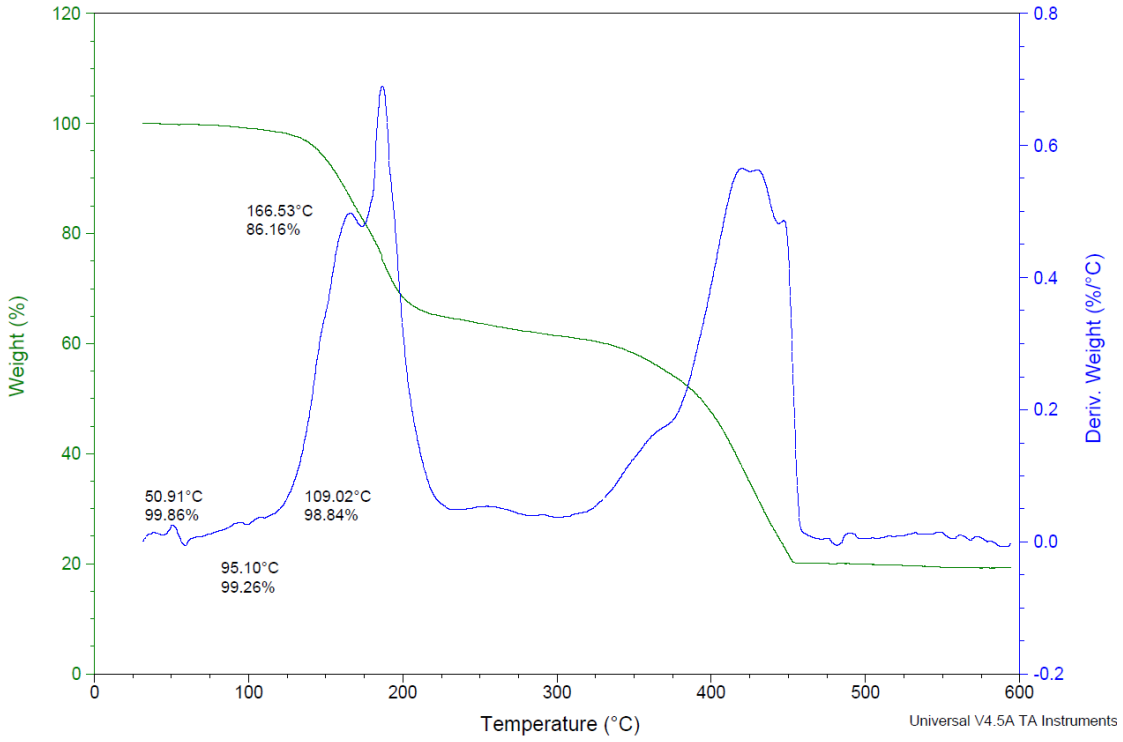

Figure S76. TGA data for complex **L1**-[Pd(allyl)Cl]

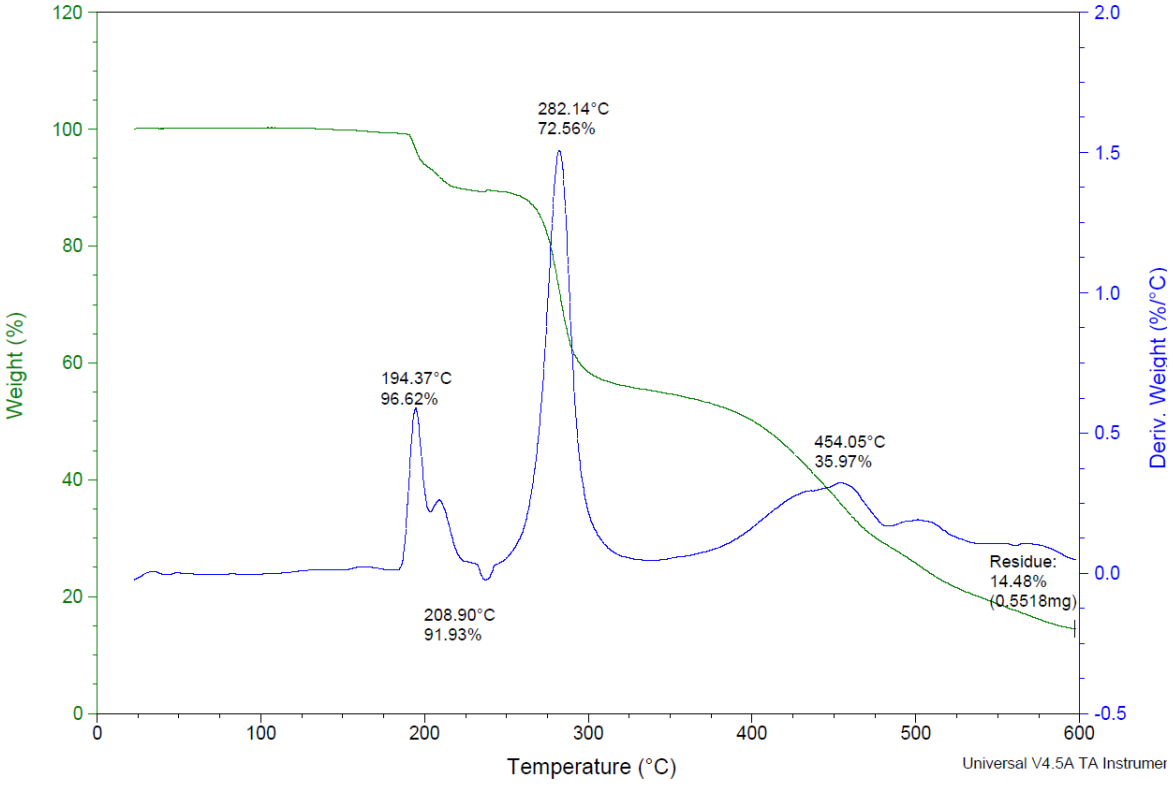

Figure S77. TGA data for complex **L2**-$[Pd(allyl)Cl]_2$

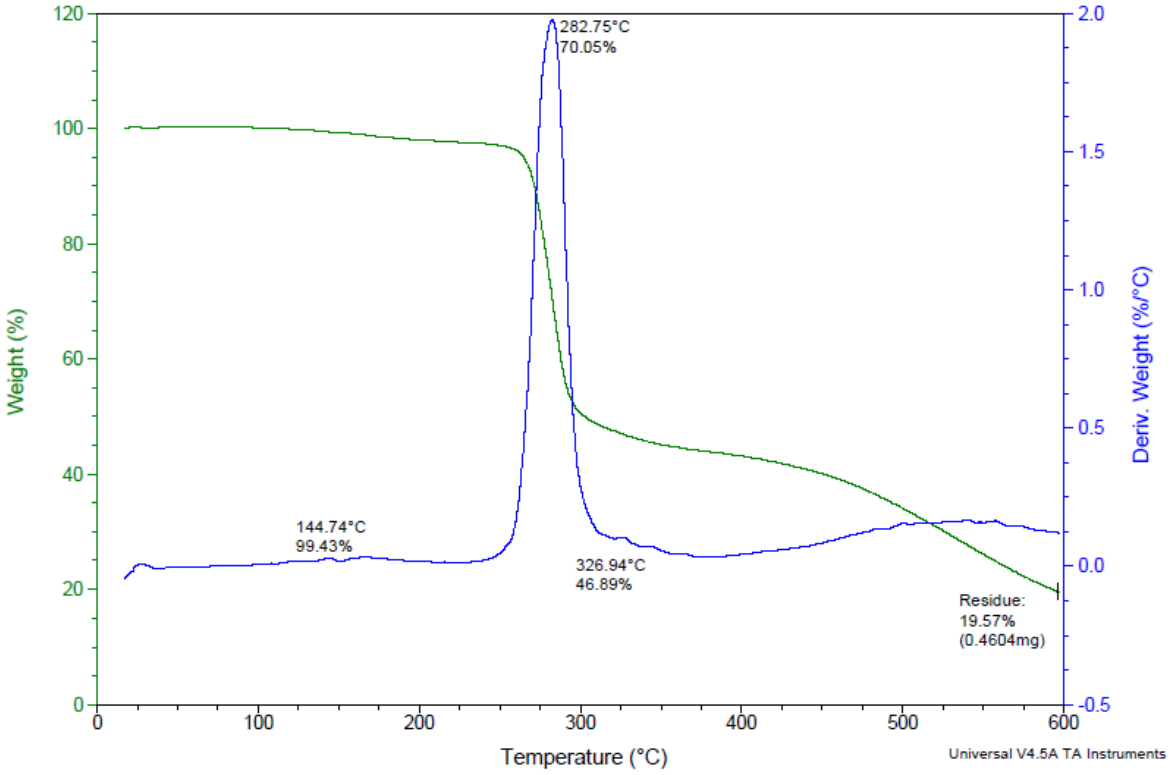

Figure S78. TGA data for complex **L3**-$[Pd(allyl)Cl]_3$

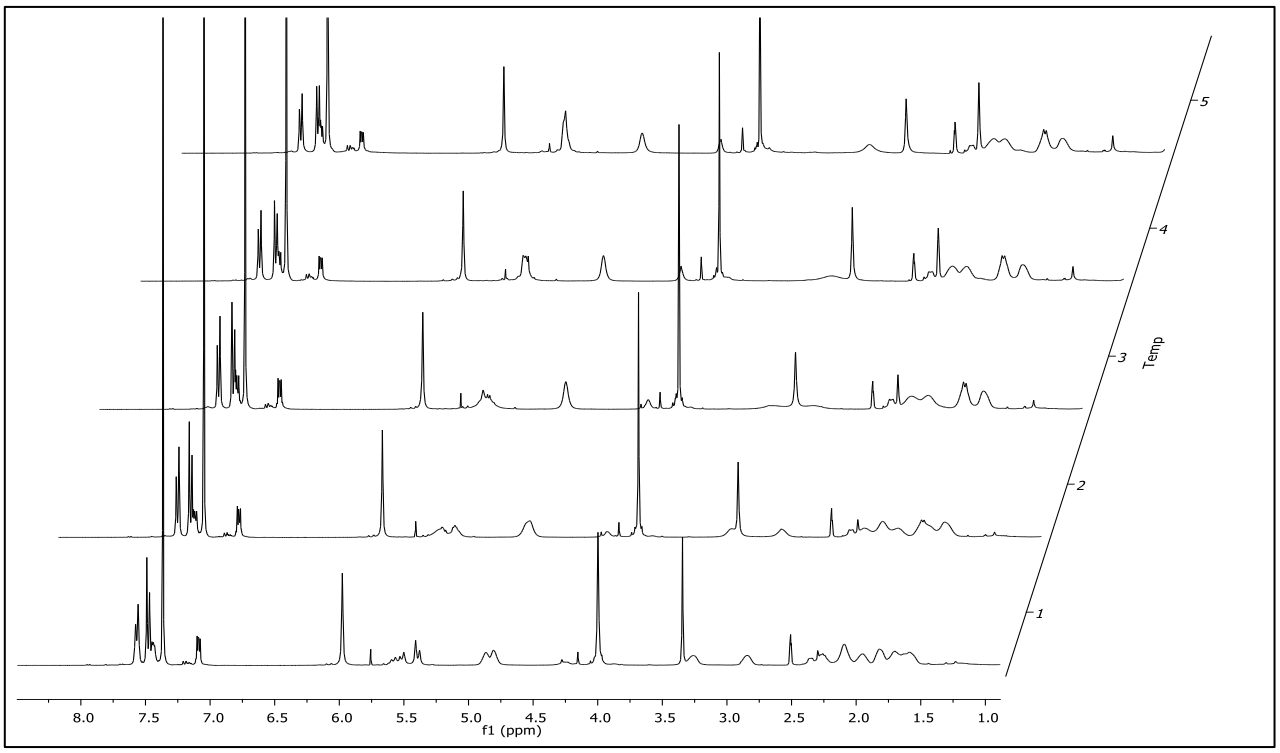

Figure S79. ^{1}H VT- NMR spectra in DMSO-$_{d6}$ for complex **L2**-[Rh(COD)Cl]$_2$. Temp **1** = 25°C; Temp **2** = 50°C; Temp **3** = 75°C; Temp **4** = 100°C; Temp **5** = 120°C

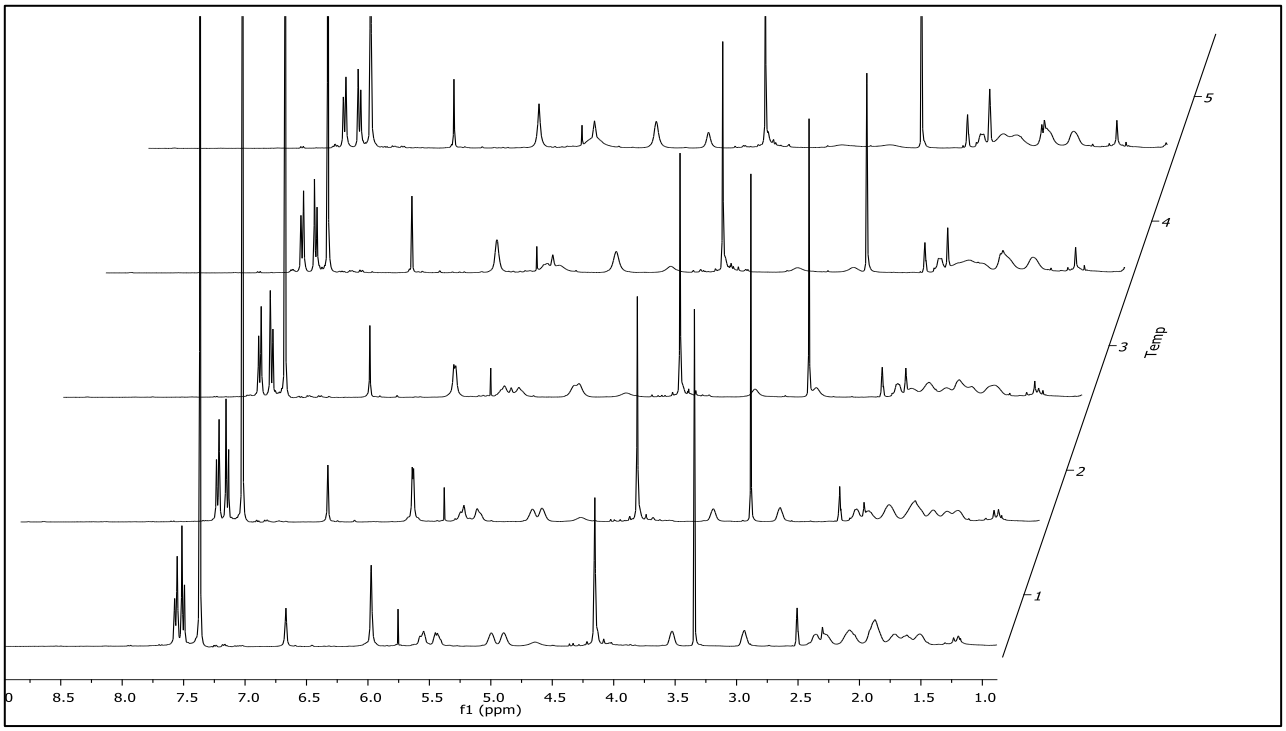

Figure S80.^{1}H VT- NMR spectra in DMSO-$_{d6}$ for complex **L3**-[Rh(COD)Cl]$_3$. Temp **1** = 25°C; Temp **2** = 50°C; Temp **3** = 75°C; Temp **4** = 100°C; Temp **5** = 120°C

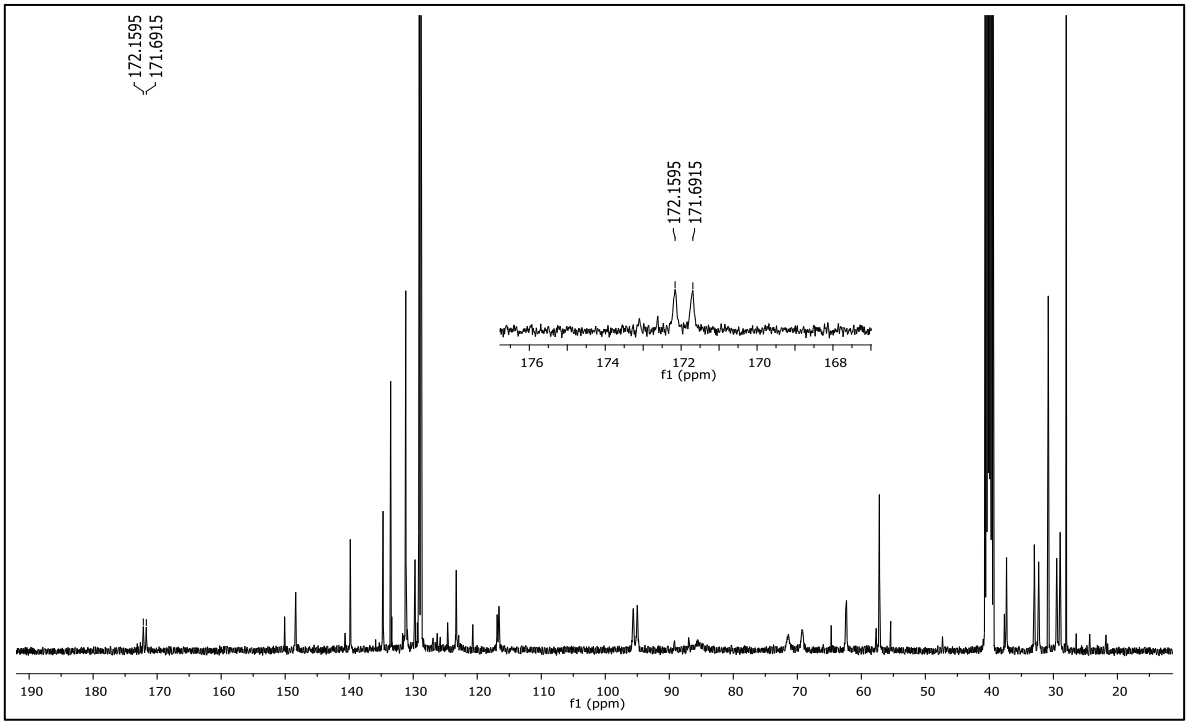

Figure S81. Room temperature ^{13}C NMR spectrum of **L2**-[Rh(COD)Cl]$_2$ in DMSO-$_{d6}$

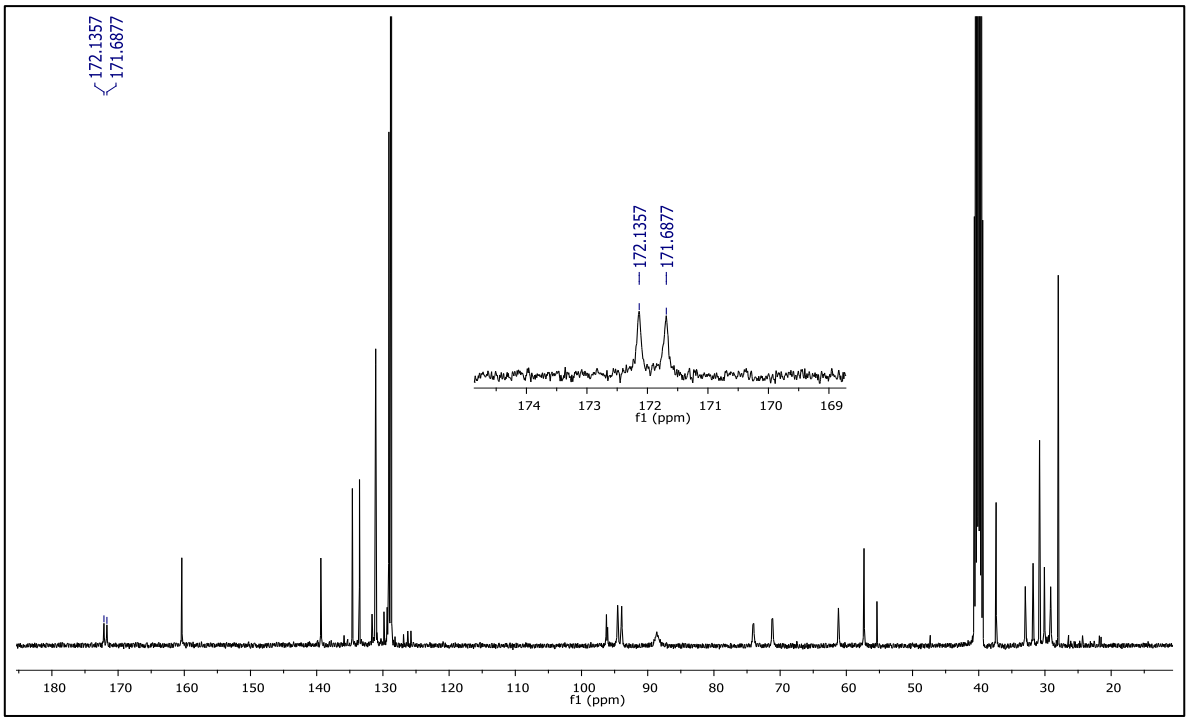

Figure S82. Room temperature ^{13}C NMR spectrum of **L3**-[Rh(COD)Cl]$_3$ in DMSO-$_{d6}$