

Electronic Supplementary Information (ESI)

Single-crystal-to-single-crystal direct cross-linking and photopolymerization of a discrete Ag(I) complex to give a 1D polycyclobutane coordination polymer

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1. Materials:

2-Chloro-5-chloromethylpyridine and Silver Chlorate were purchased from sigma-aldrich chemical company. Tert-butanol, Potassium tert-butoxide, Benzaldehyde, Triethyl phosphate, Acetonitrile and Hexane were purchased from Fischer Scientific and used as received.

2. Experimental Procedures:

Diethyl (6-chloropyridin-3-yl)methylphosphonate

In a 100 mL round bottom flask, 2-chloro-5-chloromethylpyridine (2.001 g, 12.34 mmol) was dissolved in triethyl phosphite (3.073 g, 18.51 mmol) and the red color solution was refluxed under argon for 6 h. The resulting red color liquid was distilled under vacuum to yield a red oil (2.892 g, 89% yield). ¹H NMR (DMSO-d₆, 300 MHz); 8.30 (s, 1H), 7.74 (d, J = 9 Hz, 1H), 7.45 (d, J = 9 Hz, 1H), 4.00 (m, 4H), 3.31 (d, J = 24 Hz, 2H), 1.24 (t, J=6 Hz, 6H). ¹³C NMR (CDCl₃, 75 MHz); 150.9, 149.0, 141.2, 128.9, 124.3, 62.1, 61.5, 29.8, 28.1, 16.6.

trans-1-(4-Cl-3-pyridyl)-2-(phenyl)ethylene (Cl-pyr-pe)¹

A mixture of diethyl (6-chloropyridin-3-yl)methylphosphonate (1.001 g, 3.79 mmol) and benzaldehyde (0.402 g, 3.79 mmol) were loaded in a 100 mL round bottom flask under argon. The solution was diluted with tert-butanol (2.00 mL). Potassium tert-butoxide (0.630 g, 5.61 mmol) was added to the solution slowly in portions over 20 min while stirring vigorously. Immediate reaction was observed resulting in rapid increase in temperature of the flask. The temperature was not allowed to increase beyond 40 °C using an ice-water bath. After 2 h, the resulting brown semi-solid was added to ice-cold water (50 mL) and stirred for 30 min. The beige color solid that precipitated out of the solution was filtered under vacuum and washed with excess water. The solid was dried at room temperature and recrystallized from boiling hexane to yield a white crystalline solid

(0.581 g, 71% yield) ^1H NMR (CDCl_3 , 300 MHz): 8.45 (d, $J=3$ Hz, 1H), 7.76 (dd, $J=3, 9$ Hz, 1H), 7.50 (m, 2H), 7.38-7.28 (m, 4H) 7.12 (d, $J=18$ Hz, 1H), 7.00 (d, $J=18$ Hz, 1H). ^{13}C NMR (CDCl_3 , 75 MHz): 149.8, 148.1, 136.3, 135.3, 132.0, 131.5, 128.8, 128.5, 126.7, 124.2, 123.3. HRMS (ESI): calculated for $\text{C}_{13}\text{H}_{10}\text{N}_1\text{Cl}_1$: $[\text{M}+\text{H}]^+$ 216.0574: found 216.0597.

Synthesis of $[\text{Ag}_2(\text{Cl-pyr-pe})_4(\text{ClO}_3)_2]$ (1)

Cl-pyr-pe (0.160 g, 0.74 mmol) and silver chlorate (0.071 g, 0.37 mmol) were dissolved in dry acetonitrile (1 mL) separately. The two solutions were mixed and the resulting solids upon mixing (if any) were re-dissolved upon heating. The hot solution was cooled down to room temperature and filtered in a 20 mL glass vial. The vial was wrapped in with aluminum foil and allowed to stand at room temperature in dark for 24-48 hours. Colorless crystals separated from the solution within 24-48 hours. The crystals were separated from the solution by vacuum filtration and allowed to dry in air in absence of light (0.212 g, 92% yield). ^1H NMR (DMSO-d_6 , 400 MHz): 8.64 (d, $J = 4\text{Hz}$, 1H), 8.15 (dd, $J = 2, 8$ Hz, 1H), 7.65(d, $J = 8$ Hz, 1H), 7.55(d, $J = 8$ Hz, 1H), 7.42-7.48(m, 3H), 7.29-7.36 (m, 2H). ^{13}C NMR (DMSO-d_6 , 100 MHz): 149.2, 148.7, 136.9, 136.7, 132.8, 131.8, 129.2, 128.7, 127.2, 124.7, 123.9. MS (ESI): calculated for $\text{C}_{26}\text{H}_{20}\text{N}_2\text{Cl}_2\text{Ag}_1$: $[\text{M}]^+$ 537.0: found 537.0.

Synthesis of $[\text{Ag}_2(\text{Cl-pyr-pe})_2(\text{Cl-pyr-p-cb})(\text{ClO}_3)_2]$ 2

$[\text{Ag}_2(\text{Cl-pyr-pe})_4(\text{ClO}_3)_2]$ (1) was powdered and placed in between two pyrex glass plates. The powdered sample was irradiated by UV light sourced from a medium pressure broadband mercury lamp for 24 hours. The colorless solid become yellow-brown in color upon photoreaction. Te powder was scraped out of the glass plates and characterized by ^1H NMR and ^{13}C NMR spectroscopy. ^1H NMR (DMSO-d_6 , 400 MHz): 8.88 (s), 8.59 (s), 8.25 (m), 8.11 (d), 7.93 (d), 7.66-7.06 (m), 4.64 (m), 4.56 (m). ^{13}C NMR (DMSO-d_6 , 100

MHz): 150.1, 148.7, 148.3, 139.6, 135.9, 131.8, 129.2, 128.6, 128.4, 127.2, 126.7, 124.8, 123.9, 46.1, 43.3.

X-ray crystallography

All crystal data were measured on a Nonius Kappa CCD single-crystal X-ray diffractometer at room temperature using MoKa radiation ($\lambda = 0.7107 \text{ \AA}$). After anisotropic refinement of non-hydrogen atoms, H atoms bonded to C atoms were placed in idealized positions and allowed to ride on the atom to which they are attached. Structure solutions were accomplished using SHELXS-97, while structure refinements were conducted using SHELXL-97.²

Single-crystal to single-crystal synthesis of 2

A suitable single crystal of **1** was chosen to characterize it *via* single crystal X-ray spectroscopy. When the data collection was completed, the crystal was carefully placed in between two petri-dishes under argon and sealed with teflon tapes. The crystal was transferred into the photoreactor and irradiated with UV-light for 24 hours. The crystal appeared intact on plain eye but under microscope there were some small cracks detected but the crystal was good enough to be characterized by single crystal-X ray spectroscopy.

3. Spectral Data:

¹H NMR spectra were recorded using a Varian Merc 300 NMR spectrometer operating at 300 MHz and 400 MHz. ¹³C NMR spectra were recorded at the same instrument with a calculated operating frequency of 75 MHz and 100 MHz. The data were processed using MestReNova (version 6.2.0) desktop NMR data processing software.³

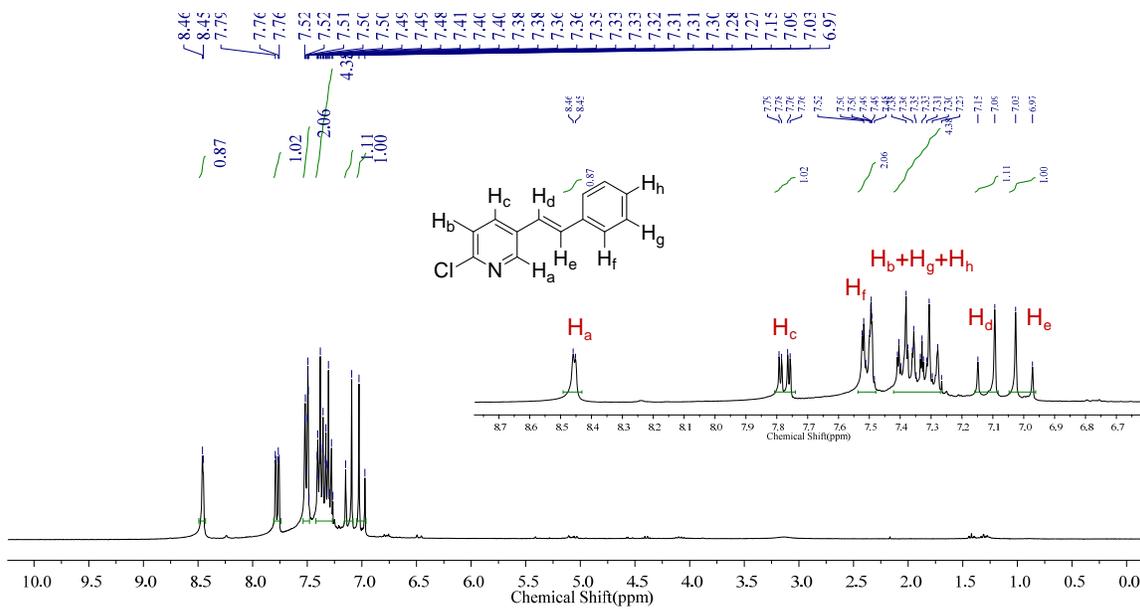


Fig. 1. ^1H NMR spectrum of Cl-pyr-pe in CDCl_3 with peak assignments (inset).

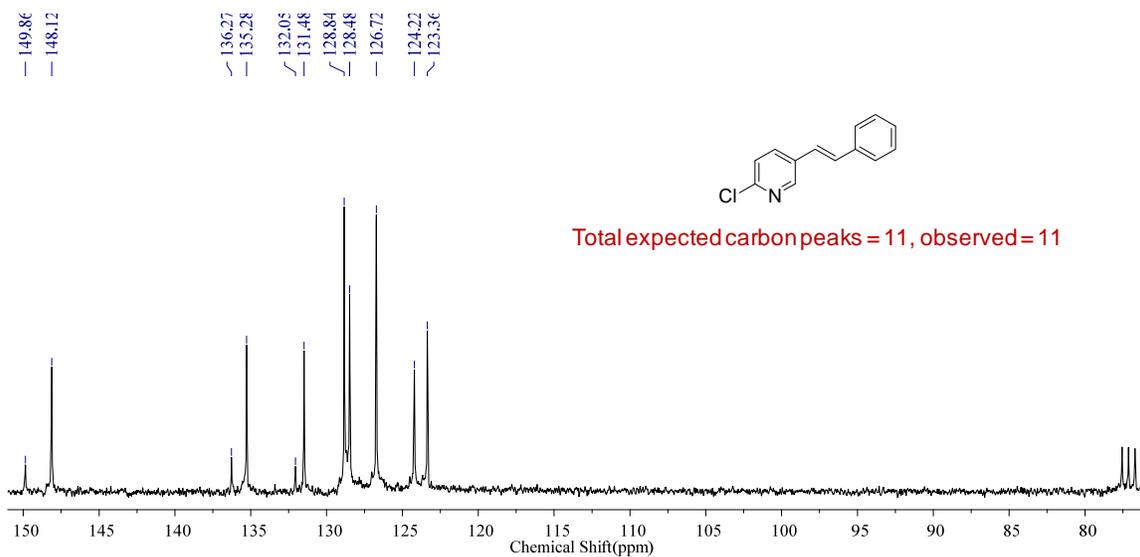


Fig. 2. ^{13}C NMR spectrum of Cl-pyr-pe in CDCl_3 .

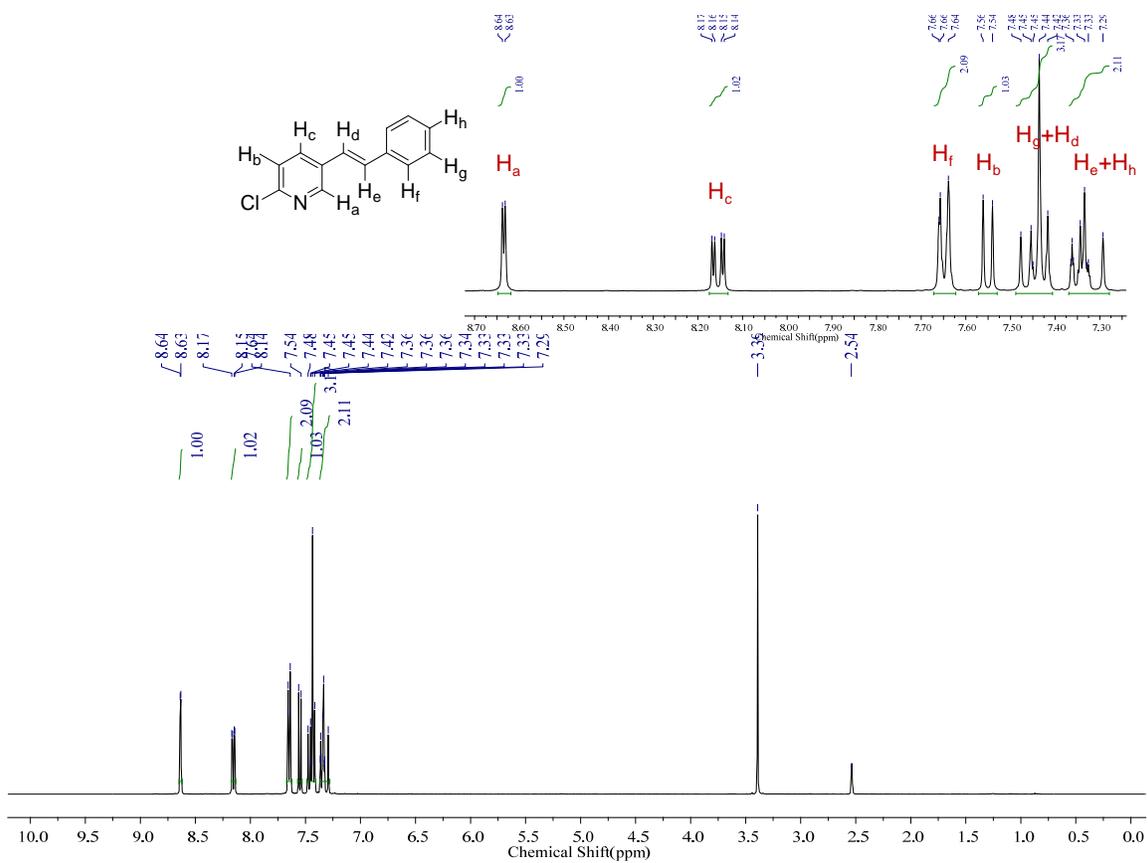


Fig. 3. ¹H NMR spectrum of **1** in DMSO-d₆ with peaks assignments (inset).

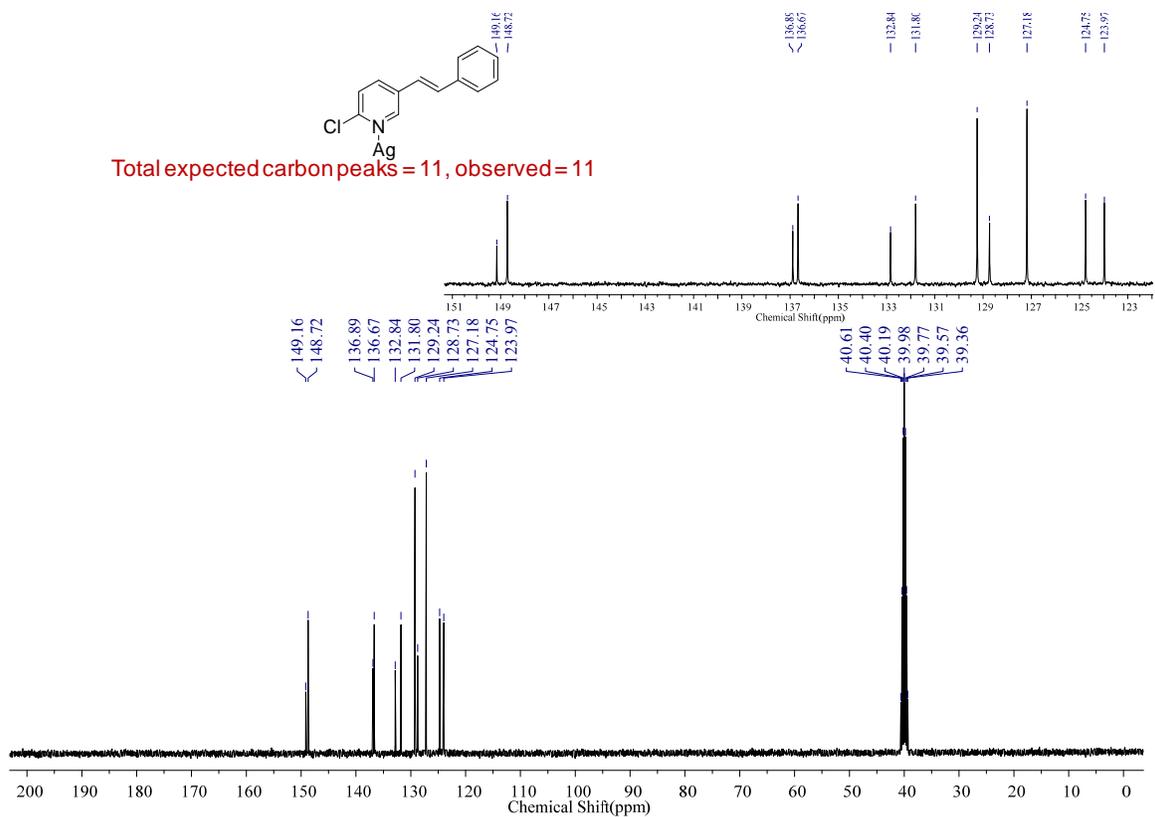


Fig. 4. ^{13}C NMR spectrum of **1** in DMSO-d_6 .

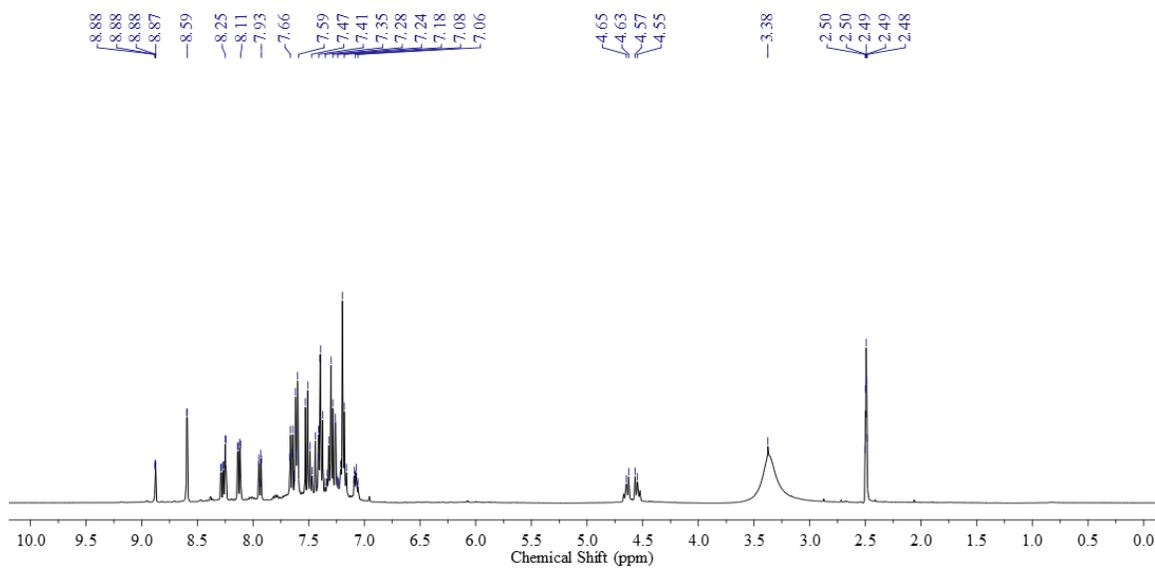


Fig. 5. ^1H NMR spectrum of **2** in DMSO-d_6 .

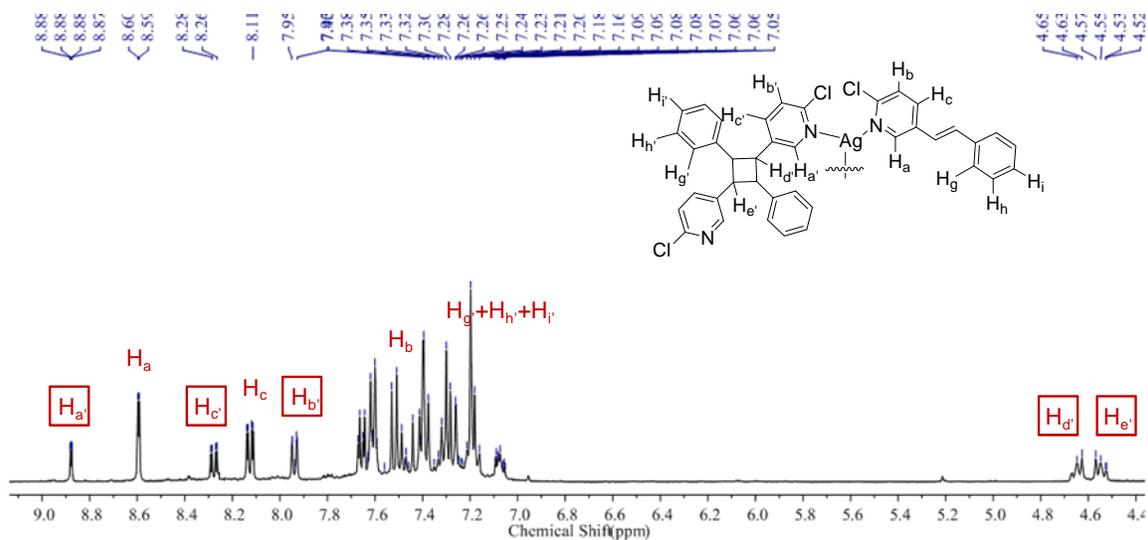


Fig. 6. ^1H NMR spectrum (expanded view) of **2** in DMSO-d_6 with partial peak assignments (peaks appeared upon photoreaction are highlighted in red boxes).

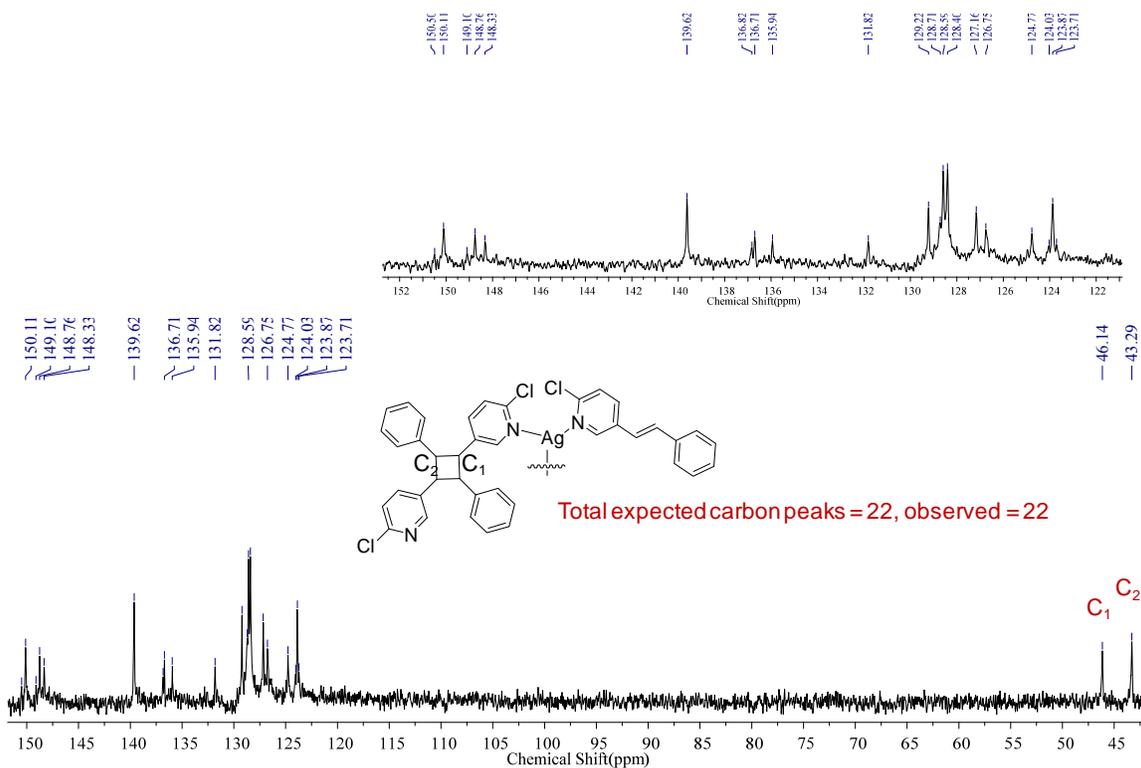


Fig. 7. ^{13}C NMR spectrum of **2** in DMSO-d_6 .

4. Diffraction Data:

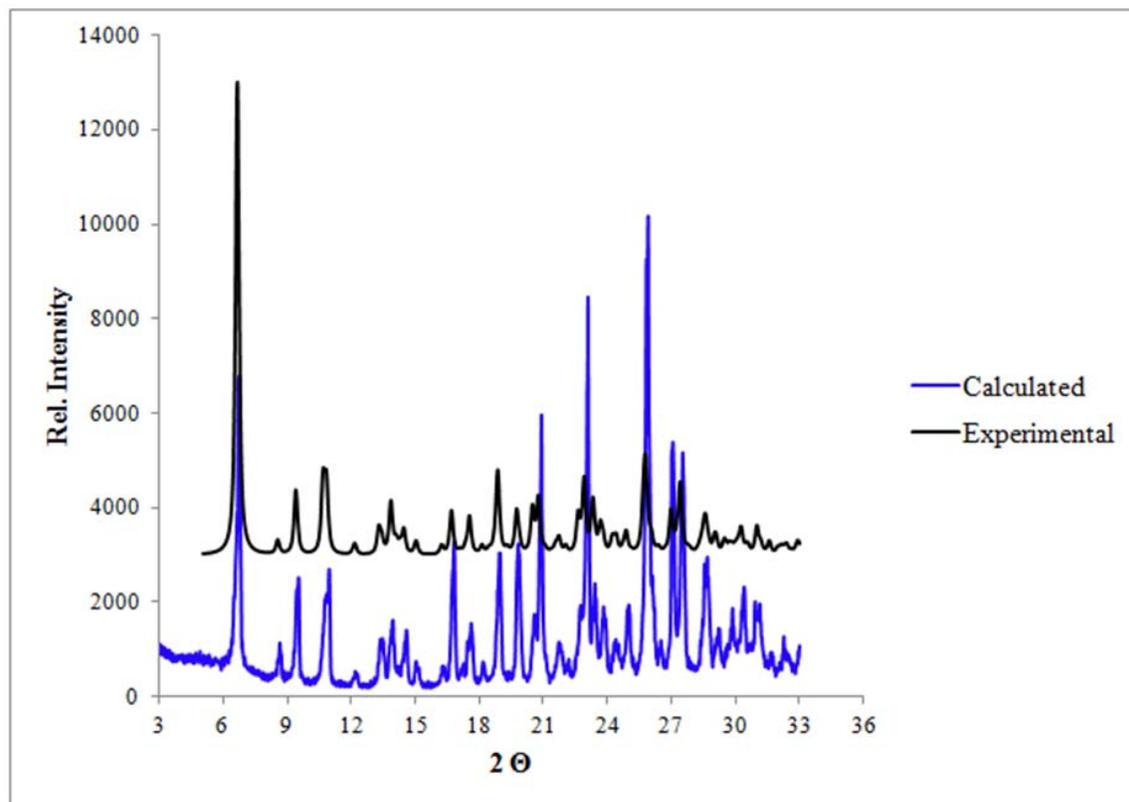


Fig 8. Powder x-ray diffraction of **1**: Overlay of calculated and experimental patterns.

6. References:

1. J. B. Arterburn, C. Corona, K. V. Rao, K. E. Carlson, J. A. Katzenellenbogen *J. Org. Chem.* **2003**, *68*, 7063.
2. G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112.
3. MestReNova 6.2.0, Mestrelab Research S. L.