

Supporting Information

Photogeneration of Hydrogen from Water Using an Integrated System Based on TiO₂ and Platinum (II) Diimine Dithiolate Sensitizers

Jie Zhang, Pingwu Du, Jacob Schneider, Paul Jarosz, and Richard Eisenberg*

Department of Chemistry, University of Rochester, Rochester, New York 14627

Experimental Procedures.

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Experimental Procedure

General information for synthesis and characterization

Mercuric acetate, lithium methoxide, 1,2-benzenedithiol, and chloroplatinic acid hexahydrate were purchased from Aldrich and used without further purification. Titanium dioxide is a Degussa product (Degussa P25) and was used as received. Pt(dbbpy)Cl₂ (dbbpy = 4,4'-di-*tert*-butyl-2,2'-bipyridine),¹ Pt(ecbpy)Cl₂ (ecbpy = 4,4'-bis(ethoxycarbonyl)-2,2'-bipyridine),² Pt(dcbpy)Cl₂ (dcbpy = 4,4'-dicarboxyl-2,2'-bipyridine)³ and 4,5-dicarbomethoxy-1,3-dithiol-2-thione⁴ were prepared according to literature procedures. Syntheses were performed under nitrogen with degassed solvents that were purified by passing the degassed solvent through columns containing activated molecular sieves and activated alumina.

Infrared spectra were obtained from KBr pellets using a Shimadzu 8400 S FT-IR spectrometer. ¹H NMR (400 MHz) and ¹³C NMR (100.62 MHz) spectra were recorded on a Bruker Avance-400 spectrometer. Mass determinations were accomplished by atmospheric pressure chemical ionization (APCI) mass spectrometry using a Hewlett-Packard Series 1100 mass spectrometer (model A) equipped with a quadrupole mass filter. Absorption spectra were recorded using a Hitachi U2000 scanning spectrophotometer (200-1100 nm). Elemental analyses were carried out by Quantitative Technologies Inc. (Whitehouse, New Jersey).

Synthesis of Pt(dcbpy)(met) (1) (dcbpy = 4,4'-dicarboxyl-2,2'-bipyridine; met = *cis*-1,2-dicarbomethoxyethylene-1,2-dithiolate)

Mercuric acetate (75 mg, 0.24 mmol) and 4,5-dicarbomethoxy-1,3-dithiol-2-thione (50 mg, 0.20 mmol) were put into a 25 mL flask and 5 mL of THF/methanol (1:1 v/v) was added. The mixture was stirred overnight until a black precipitate formed. The solution was filtered yielding a slightly yellow filtrate containing 4,5-dicarbomethoxy-1,3-dithiol-2-one. To this filtrate was added LiOMe (17 mg, 0.45 mmol), and the mixture was stirred at room temperature for 10 minutes. The resulting solution containing the lithium salt of *cis*-1,2-dicarbomethoxyethylenedithiolate (Li₂met) was used directly in the following experiment.

Pt(dcbpy)Cl₂ (100 mg, 0.20 mmol) was put into a 50 mL flask and 30 mL of THF/H₂O (1:1 v/v) were added. Addition of NaOH aqueous solution (0.1 M) proceeded dropwise until

Pt(dcbpy)Cl₂ was dissolved completely. To the resulting solution was added the lithium salt of *cis*-1,2-dicarbomethoxyethylenedithiolate (Li₂met) as made in the above experiment. The mixture was stirred at room temperature for 5 hours and a deep purple solution was formed. The solution was filtered. After THF was removed from the filtrate, HCl (0.1 M) was added and blue color precipitate formed. The precipitate was collected, washed with water and ether for several times and dried, and Pt(dcbpy)(met) was obtained (85 mg, 0.13 mmol, yield 66% base on Pt). ¹H NMR (DMSO-*d*₆): δ 14.30 (s, 2H), 9.16 (d, 2H, J = 6 Hz), 8.95 (s, 2H), 8.09 (d, 2H, J = 6 Hz), 3.65 (s, 3H). ¹³C{¹H} NMR (DMSO-*d*₆): δ 165.99, 165.17, 156.15, 149.24, 141.16, 135.89, 128.49, 124.94, 52.48. FT-IR (KBr): 3000 (br, OH), 1700 (s, C=O), 1720 (s, C=O) cm⁻¹. MS (APCI): *m/z* 645.8 (M⁺). Anal. Calcd for C₁₈H₁₄N₂O₈PtS₂: C, 33.49; H, 2.19; N, 4.34. Found: C, 34.20; H, 2.46; N, 3.91.

Synthesis of Pt(dcbpy)(bdt) (2) (dcbpy = 4,4'-dicarboxyl-2,2'-bipyridine; bdt = 1,2-benzenedithiolate)

Pt(dcbpy)Cl₂ (100 mg, 0.20 mmol) was placed in a 50 mL flask and 30 mL of THF/H₂O (1:1 v/v) were added. Addition of NaOH aqueous solution (0.1 M) proceeded dropwise until Pt(dcbpy)Cl₂ was dissolved completely. To the resulting solution was added 1,2-benzenedithiol (0.25 mmol). The mixture was stirred at room temperature overnight. After THF was removed, HCl (0.1 M) was added and a blue colored precipitate formed. The precipitate was collected, washed with water, THF and ether several times and dried, yielding Pt(dcbpy)(bdt) as the product (90 mg, 0.15 mmol, yield 78% based on Pt). ¹H NMR (DMSO-*d*₆): δ 14.27 (s, 2H), 9.25 (d, 2H, J = 6 Hz), 8.95 (s, 2H), 8.11 (d, 2H, J = 6 Hz), 7.21 (dd, 2H, J = 3 Hz, J = 2 Hz), 6.71 (dd, 2H, J = 3 Hz, J = 2 Hz). ¹³C{¹H} NMR (DMSO-*d*₆): δ 165.30, 155.99, 149.13, 143.04, 140.52, 128.34, 127.92, 124.73, 122.07. FT-IR (KBr): 3000 (br, OH), 1700 (s, C=O) cm⁻¹. MS (APCI): *m/z* 579.8 (M⁺). Anal. Calcd for C₁₈H₁₂N₂O₄PtS₂: C, 37.31; H, 2.09; N, 4.83. Found: C, 37.55; H, 2.01; N, 4.41.

Synthesis of Pt(dbbpy)(met) (3) (dbbpy = 4,4'-di-*tert*-butyl-2,2'-bipyridine; met = *cis*-1,2-dicarbomethoxyethylene-1,2-dithiolate)

Pt(dbbpy)Cl₂ (40 mg, 0.075 mmol) was placed in a 50 mL flask and 30 mL of acetone was added. To the resulting solution was added lithium salt of *cis*-1,2-dicarbomethoxyethylenedithiolate (0.08 mmol) prepared as described in the preparation of compound (1). The solution was stirred at 50 °C overnight and then the solvent was removed. The resulting residue was dissolved in 5 mL of CH₂Cl₂ and filtered through a small quantity of silica gel eluting with CH₂Cl₂. After removing CH₂Cl₂, a dark red solid was obtained. The solid was recrystallized from CH₂Cl₂/hexane to obtain Pt(dbbpy)(met) (25 mg, 0.037 mmol, yield 50% based on Pt). ¹H NMR (acetone-*d*₆): δ 8.99 (d, 2H, J = 6 Hz), 8.60 (s, 2H), 7.79 (d, 2H, J = 6 Hz), 3.69 (s, 3H), 1.45 (s, 9H). ¹³C{¹H} NMR (acetone-*d*₆): δ 166.14, 163.87, 155.66, 147.71, 135.50, 125.10, 121.21, 51.09, 35.67, 29.32. FT-IR (KBr): 1700 (s, C=O), 1720 (s, C=O) cm⁻¹. MS (APCI): *m/z* 669.9 (M⁺). Anal. Calcd for C₂₄H₃₀N₂O₄PtS₂: C, 43.04; H, 4.52; N, 4.18. Found: C, 42.07; H, 4.33; N, 3.95.

Synthesis of Pt(ecbpy)(bdt) (4) (ecbpy = 4,4'-bis(ethoxycarbonyl)-2,2'-bipyridine; bdt = 1,2-benzenedithiolate)

Pt(ecbpy)Cl₂ (100 mg, 0.18 mmol) was put into a 50 mL flask, and acetone (30 mL) and NaOH aqueous solution (0.1 M, 1 mL) were added. To the mixture was added 1,2-benzenedithiol (0.20 mmol). A blue colored precipitate formed instantly. The precipitate was filtered, collected, washed with water and ether for several times and dried, and Pt(ecbpy)(bdt) was obtained (70 mg, 0.11 mmol, yield 61% base on Pt). ¹H NMR (DMSO-*d*₆): δ 9.29 (d, 2H, J = 6 Hz), 8.90 (s, 2H), 8.14 (d, 2H, J = 6 Hz), 7.25 (dd, 2H, J = 3 Hz, J = 2 Hz), 6.78 (dd, 2H, J = 3 Hz, J = 2 Hz), 4.49 (q, 4H, J = 7 Hz), 1.45 (t, 6H, J = 7 Hz). ¹³C{¹H} NMR (DMSO-*d*₆): δ 163.84, 156.02, 149.23, 143.06, 139.35, 128.42, 128.00, 124.73, 122.08, 62.80, 14.45. FT-IR (KBr): 1725 (s, C=O) cm⁻¹. MS (APCI): *m/z* 635.8 (M⁺). Anal. Calcd for C₂₂H₂₀N₂O₄PtS₂: C, 41.57; H, 3.17; N, 4.41. Found: C, 40.97; H, 2.90; N, 4.27.

Synthesis of platinized TiO₂ (TiO₂/Pt)

TiO₂/Pt was synthesized by slight modification of a published procedure.⁵ K₂PtCl₆ (66 mg) was dissolved in aqueous solution of MeOH (2 M, 1 L). Then TiO₂ (1 g) was added. After the mixture was degassed by bubbling nitrogen for 20 minutes, it was exposed to UV-vis irradiation without any filter for 90 minutes while stirring. Then the resulting dark grey solid was separated from the mixture and wash with water for several times and dried. The weight percentage of Pt is 3.0%.

Experimental details for photoinduced hydrogen evolution

For photoinduced hydrogen evolution, each sample was prepared in a 50 mL round bottom flask with volume of 25 mL in acetonitrile/water (v/v = 5/1 – 1/1). Typically, the sample contained 2.0 – 3.3 × 10⁻⁵ M photosensitizer (**1** – **4**), 20 mg platinized TiO₂ (TiO₂/Pt, Pt% = 3.0%), and 12.6 mM of triethanol amine (TEOA). The pH of the solution was adjusted to pH 7 – 8. The flask was sealed with a septum and degassed by bubbling nitrogen for 20 minutes under atmosphere pressure at room temperature. Following degassing, 5 mL of nitrogen gas was removed from the flask and 5 mL of methane (760 Torr) was added to serve as an internal standard for quantitative GC analysis. The sample was then irradiated under a 200 W Mercury Xexon lamp. A filter was used to cut off the higher energy light ($\lambda < 410$ nm or $\lambda < 455$ nm) from the photolysis. The hydrogen generated from the system was measured by GC-17A (Shimadzu) using nitrogen as the carrier gas with a molecular sieve 5 Å column (30 m × 0.53 mm) and a thermal conductivity detector.

References

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- (5) Bae, E.; Choi, W.; Park, J.; Shin, H. S.; Kim, S. B.; Lee, J. S. *Journal of Physical Chemistry B* **2004**, *108*, 14093-14101.

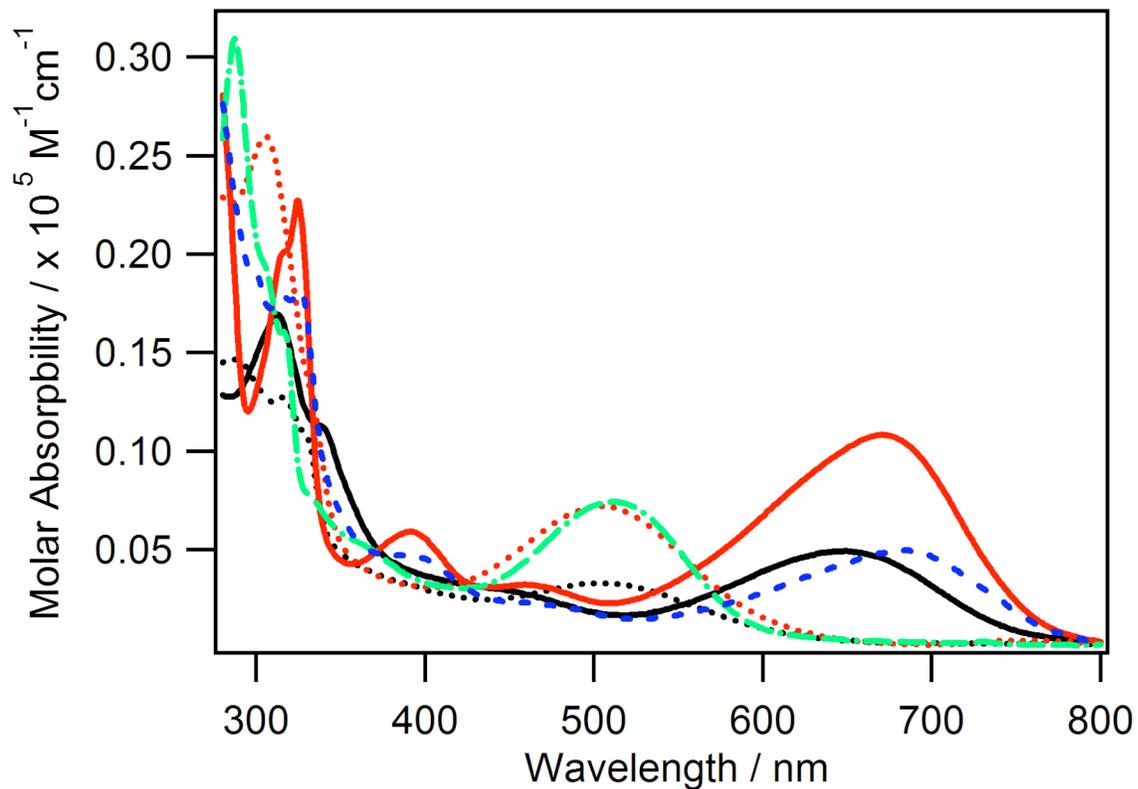


Figure S1. Absorption spectra of complexes **1-4**. Black solid line: **1** in THF/DMSO (50/1); Black dish line: **1** in H₂O/NaOH; Red solid line: **2** in THF/DMSO (50/1); Red dish line: **2** in H₂O/NaOH; Green dish line: **3** in MeCN; Blue dish line: **4** in THF/DMSO (50/1).

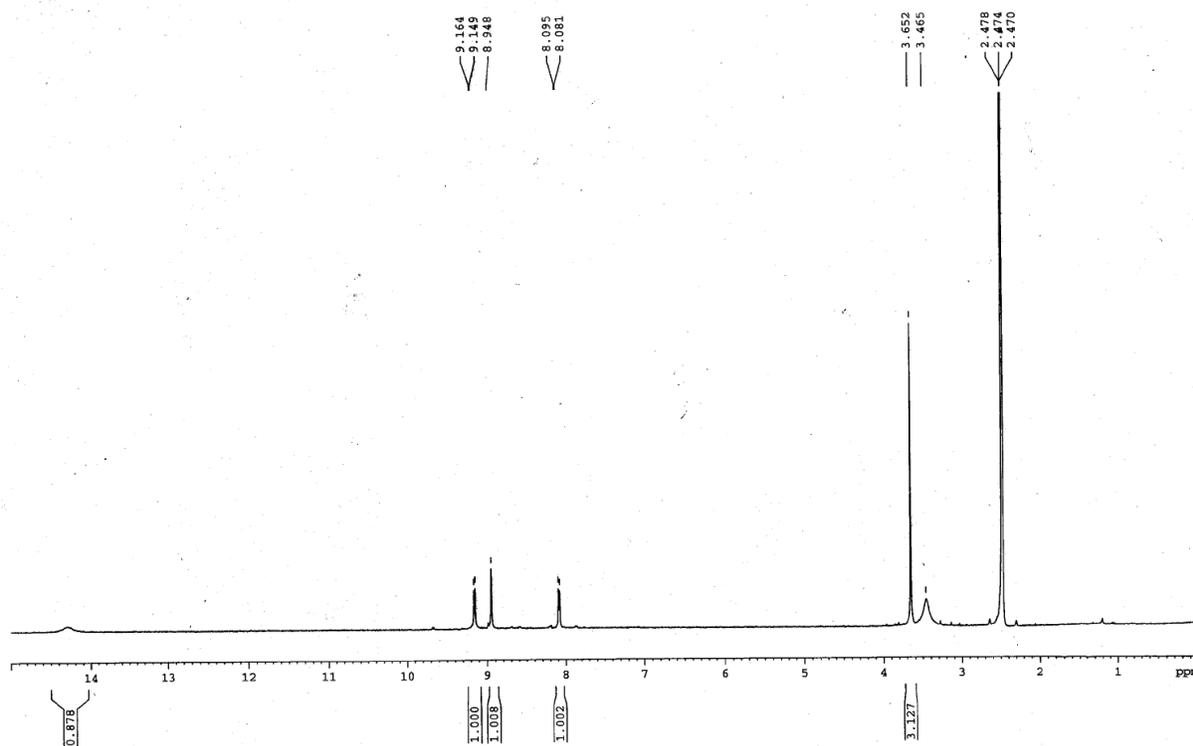


Figure S2. ¹H NMR of complex 1 in DMSO-d₆.

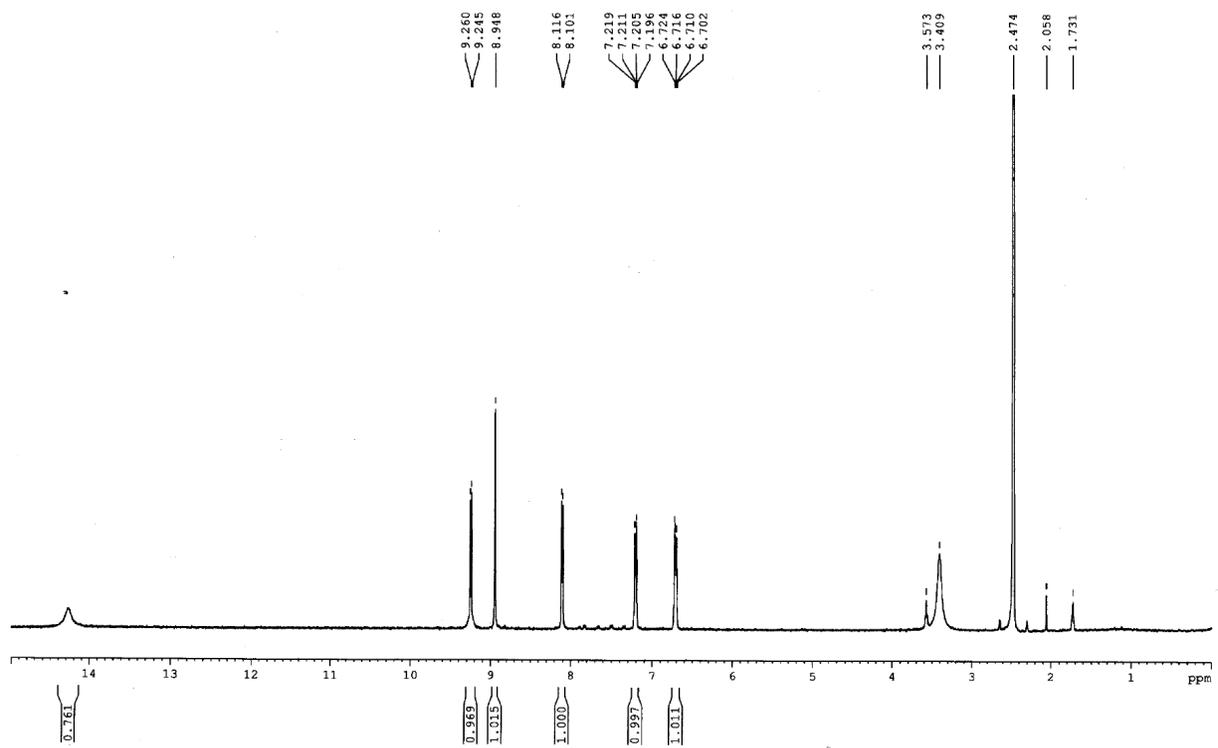


Figure S3. ^1H NMR of complex **2** in $\text{DMSO-}d_6$.

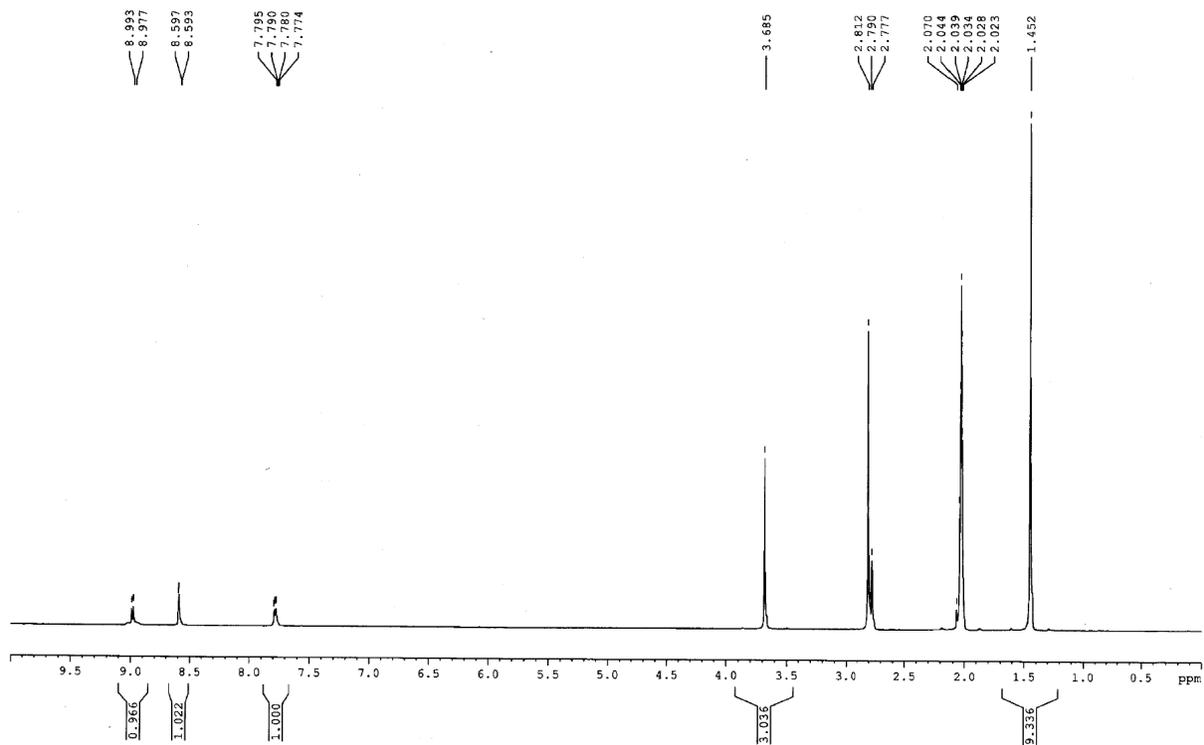


Figure S4. ^1H NMR of complex 3 in acetone- d_6 .

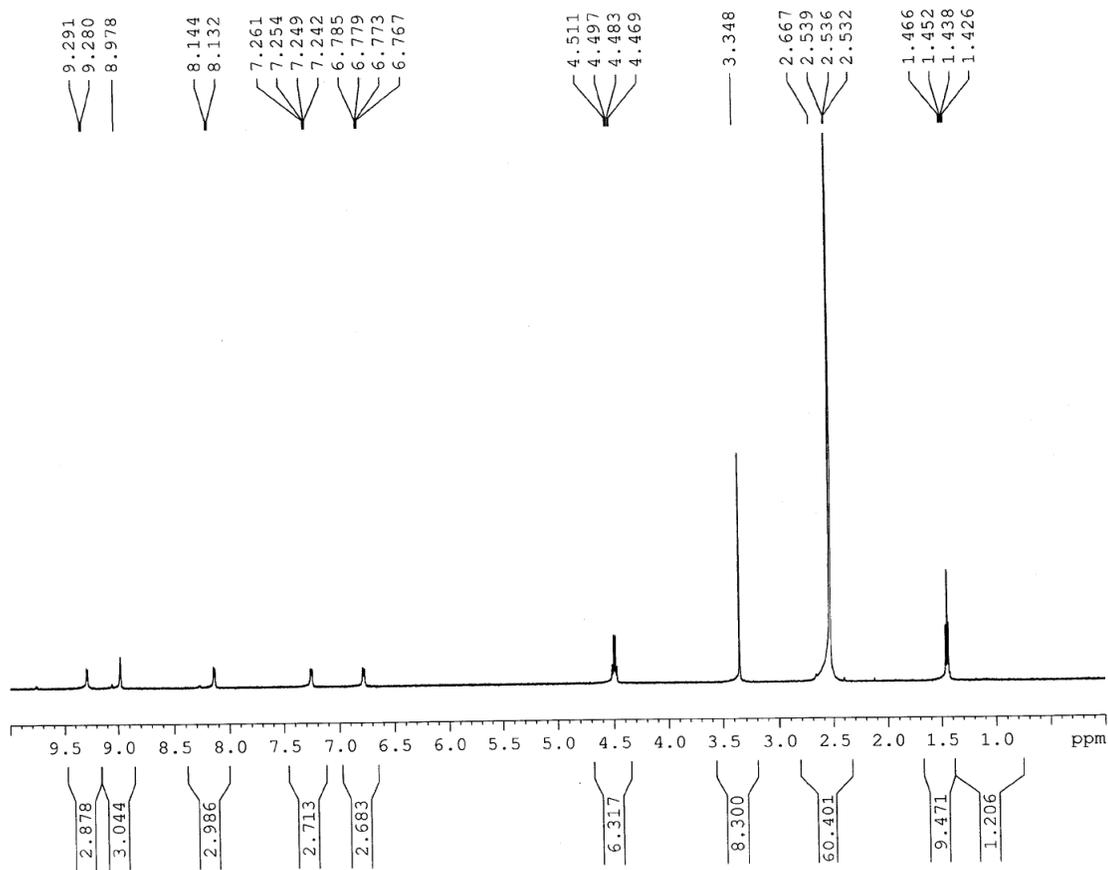


Figure S5. ¹H NMR of complex 4 in DMSO-*d*₆.

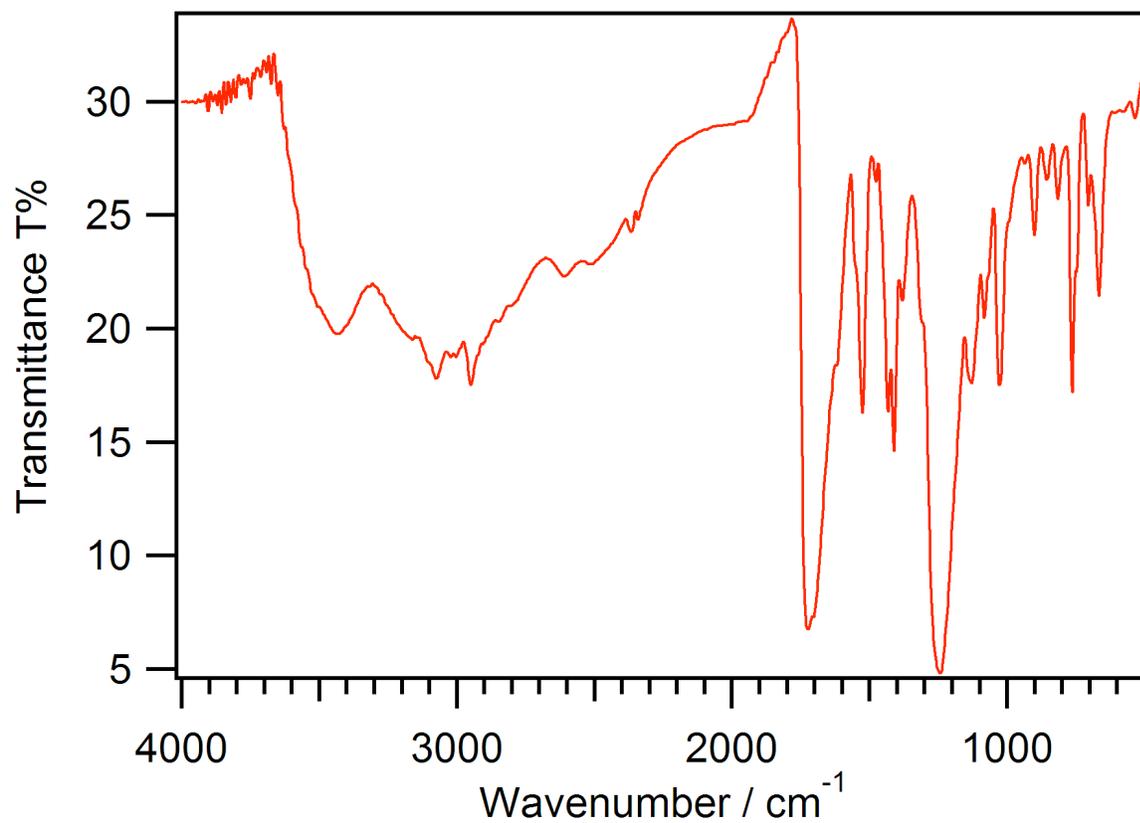


Figure S6. IR (KBr) spectra of complex **1**.

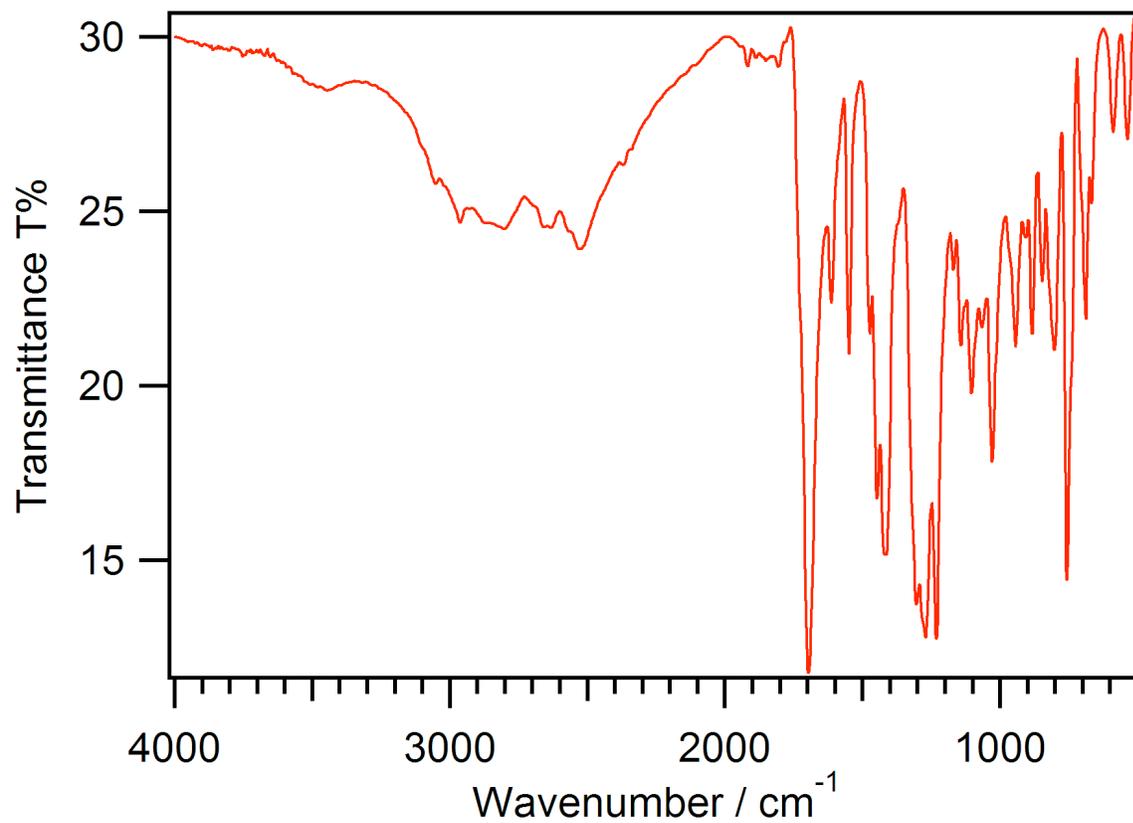


Figure S7. IR (KBr) spectra of complex 2.

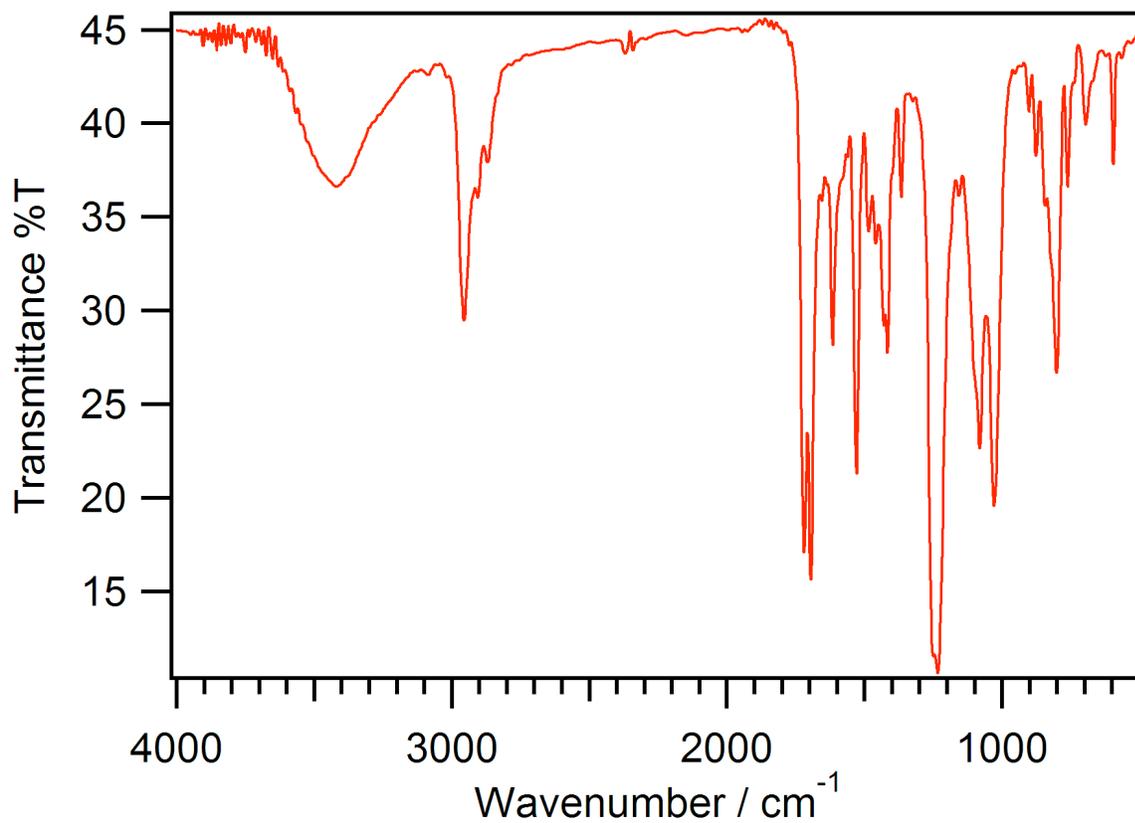


Figure S8. IR (KBr) spectra of complex **3**.

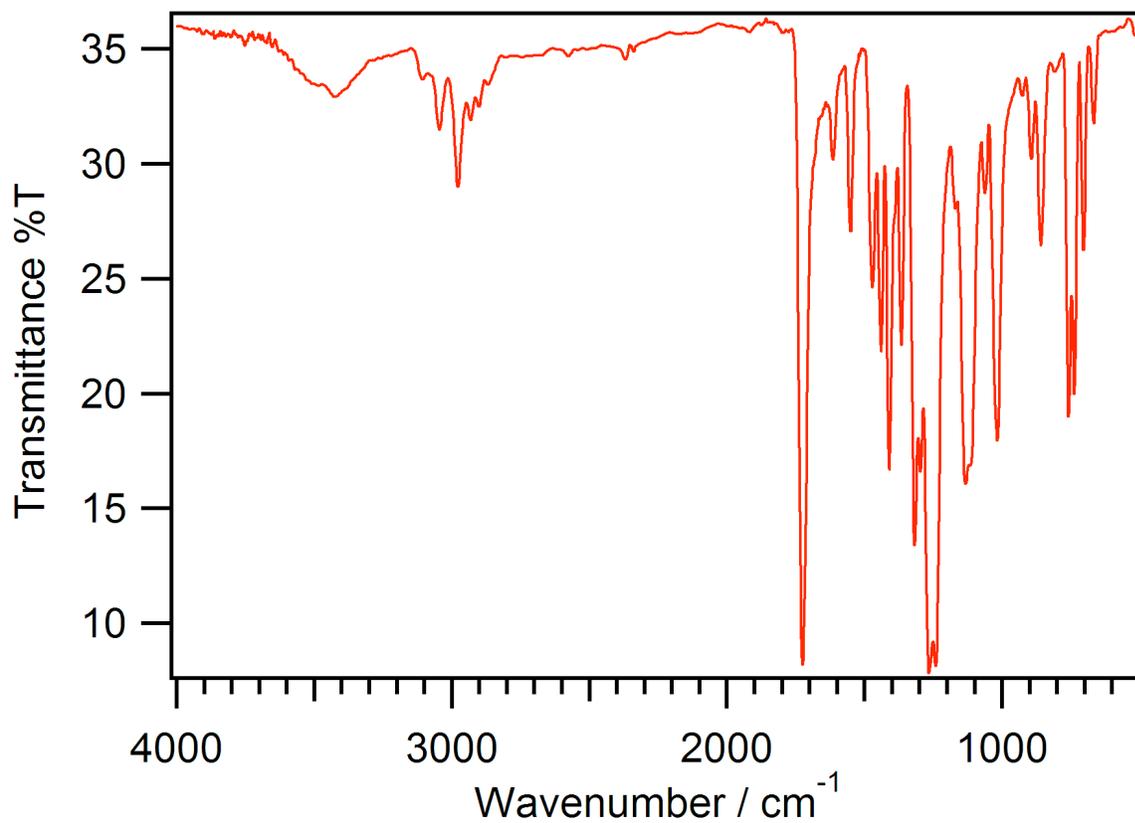


Figure S9. IR (KBr) spectra of complex **4**.

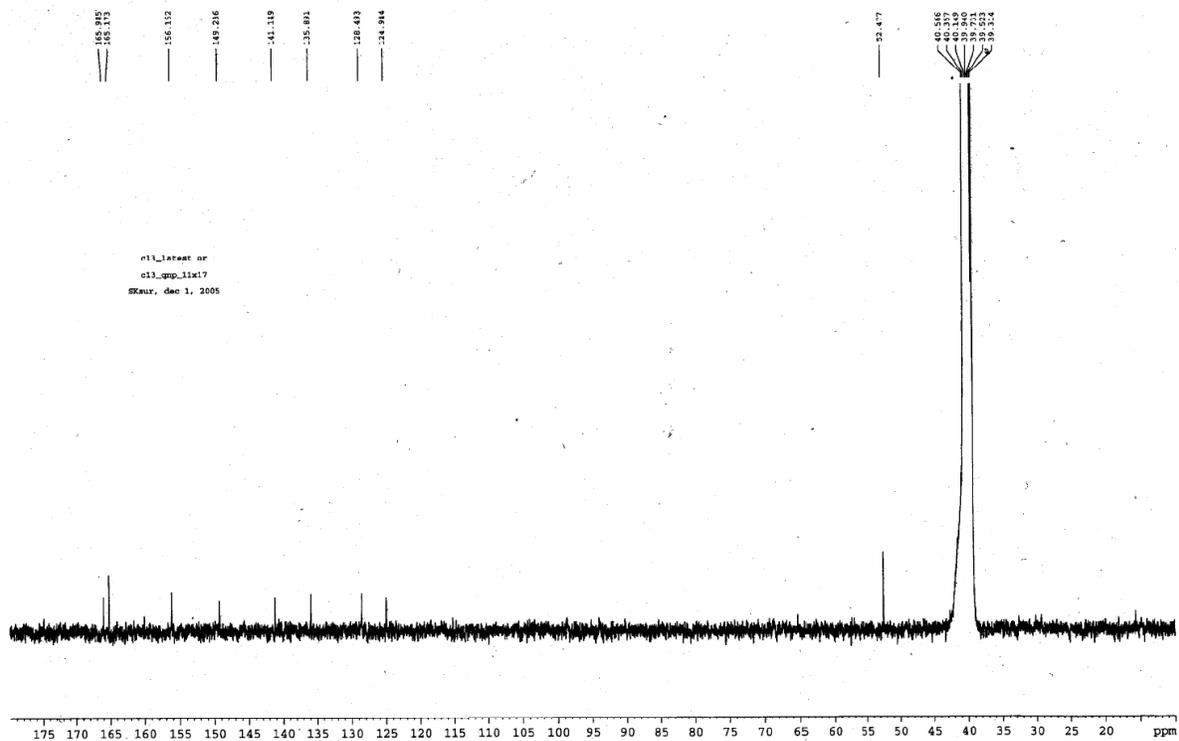


Figure S10. $^{13}\text{C}\{^1\text{H}\}$ NMR of complex **1** in $\text{DMSO-}d_6$.

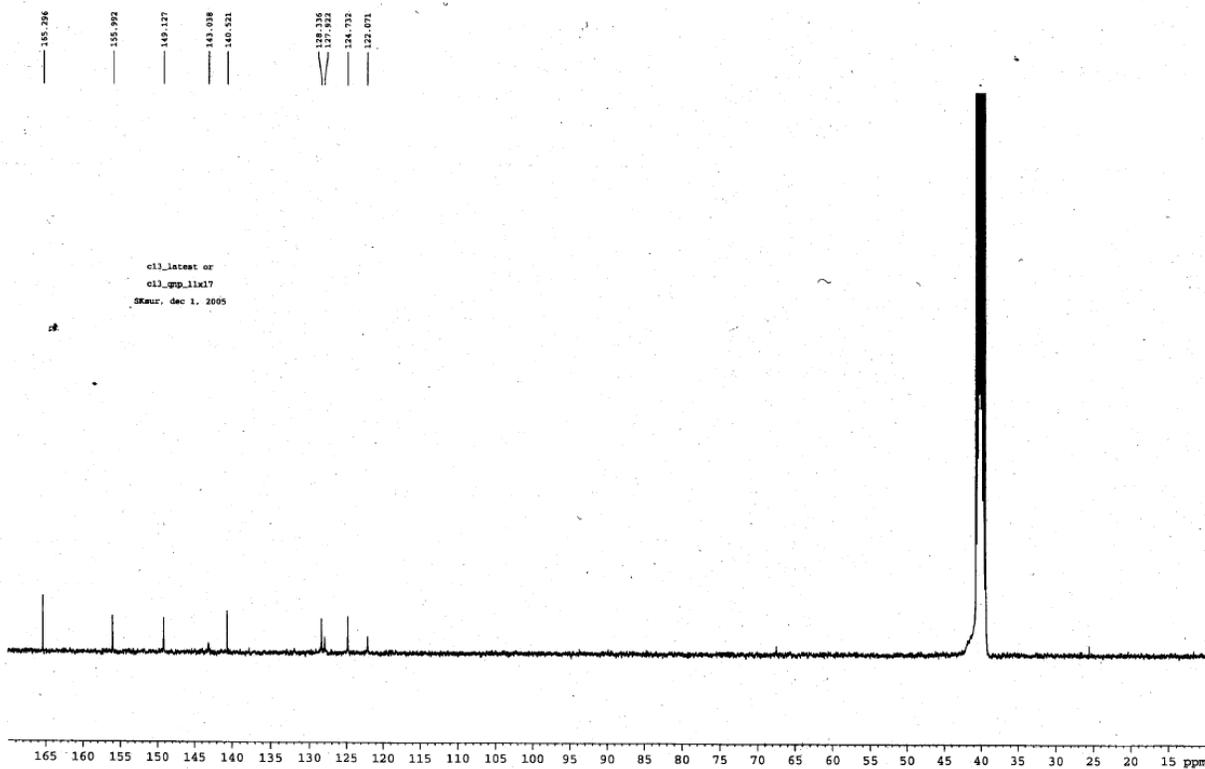


Figure S11. $^{13}\text{C}\{^1\text{H}\}$ NMR of complex **2** in $\text{DMSO-}d_6$.

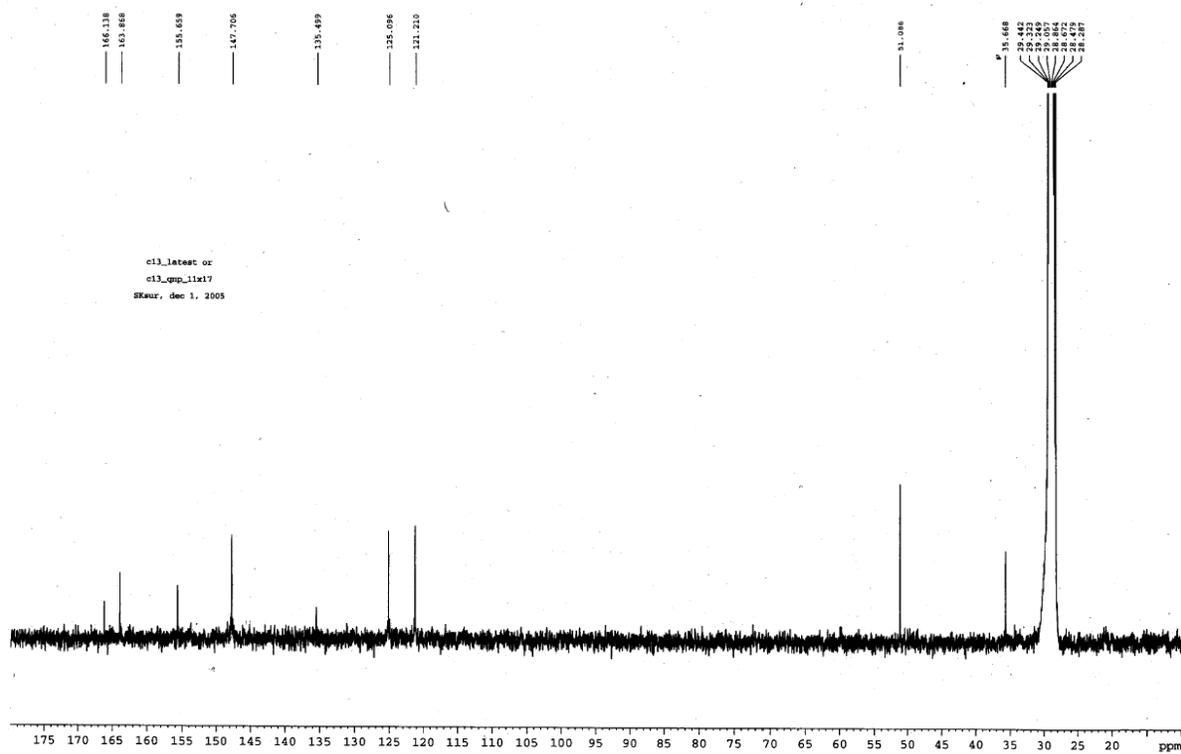


Figure S12. $^{13}\text{C}\{^1\text{H}\}$ NMR of complex **3** in acetone- d_6 .

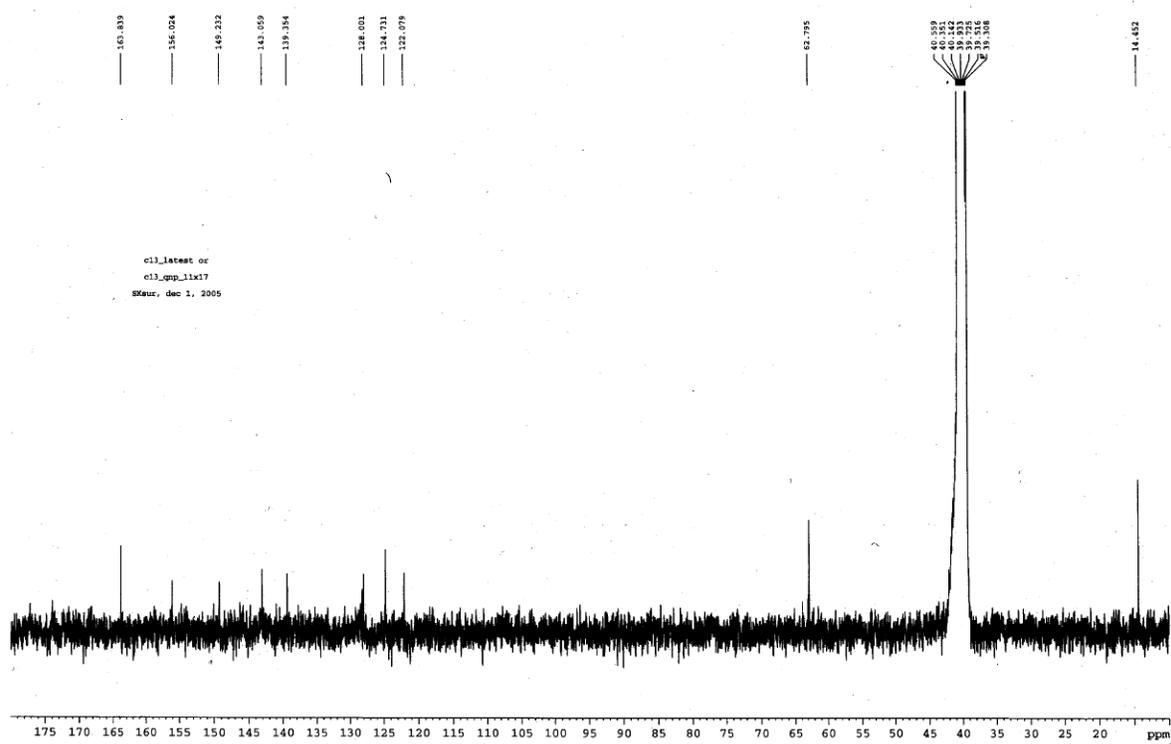


Figure S13. $^{13}\text{C}\{^1\text{H}\}$ NMR of complex 4 in $\text{DMSO-}d_6$.