Supporting Information

Triindole-Tris-Alkynyl-Bridged Trinuclear Gold(I) Complexes For Cooperative Supramolecular Self-Assembly and Small-Molecule Solution-Processable Resistive Memories

*Eugene Yau-Hin Hong and Vivian Wing-Wah Yam**

Institute of Molecular Functional Materials [Areas of Excellence Scheme, University Grants Committee (Hong Kong)] and Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, P. R. China

E-mail: wwyam@hku.hk

Experimental Section

Materials and Reagents. All commercially available reagents were of analytical grade and were used as received. All solvents were purified and distilled using standard procedures before use. *N*-Dodecyloxindole,[1] [Au(tht)Cl] (tht = tetrahydrothiophene),[2] (1,3-dimethylimidazol-2-ylidene)gold(I) chloride,[3] 1,3-bis(4-methoxybenzyl)imidazolium bromide,[4] and 2,6-dimethoxyphenyl isocyanide[5] were synthesized according to literature procedures. Tetra-*n*-butylammonium hexafluorophosphate was recrystallized at least three times from absolute ethanol before use.

Physical Measurements and Instrumentation. ^{1}H NMR spectra were recorded either on a Bruker DPX-300, a Bruker AV 400 or a Bruker DRX-500 NMR spectrometer with chemical shifts reported relative to tetramethylsilane. ^{13}C{^{1}H} NMR spectra were recorded on a Bruker AV 600 NMR spectrometer. High resolution electron impact (EI) mass spectra were recorded using a Thermo Scientific DFS High Resolution Magnetic Sector Mass Spectrometer. High resolution electrospray ionization (ESI) mass spectra were recorded on a Bruker maXis II QTOF mass spectrometer. Elemental analyses for the metal complex were performed on the Carlo Erba 1106 elemental analyzer at the Institute of Chemistry, Chinese Academy of Sciences in Beijing. UV-Vis spectra were obtained on a Varian Cary 50 UV-vis spectrophotometer. Steady-state excitation and emission spectra at room temperature and at 77 K were recorded on a Spex Fluorolog-3 model FL3-211 fluorescence spectrofluorometer equipped with an R2658P PMT detector. Photophysical measurements in low temperature glass were carried out with the sample solution

loaded in a quartz tube inside a quartz-walled Dewar flask. Liquid nitrogen was placed into the Dewar flask for low temperature (77 K) photophysical measurements. Excited-state lifetime measurements were performed using a conventional laser system. The excitation source used was the 355-nm output (third harmonic, 8 ns) of a Spectra-Physics Quanta-Ray Q-switched GCR-150 pulsed Nd:YAG laser (10 Hz). Luminescence quantum yields were measured by the optical dilute method reported by Demas and Crosby.[6] A degassed aqueous solution of quinine sulfate in 1.0 N sulfuric acid (excitation wavelength = 365 nm, $\Phi = 0.546$) was used as the reference and corrected for the refractive index of the solution.[7] All solutions for emission lifetime and luminescence quantum yield studies were degassed on a high-vacuum line in a two-compartment cell consisting of a 10-ml Pyrex bulb and a 1-cm path length quartz cuvette and sealed from the atmosphere by a Bibby Rotaflo HP6 Teflon stopper. The solutions were rigorously degassed with at least four successive freeze-pump-thaw cycles. Thermogravimetric analysis (TGA) was performed on a TA Instruments TGA Q50 thermogravimetric analyzer with a heating rate of 20 °C min^{-1} under a nitrogen atmosphere. Cyclic voltammetric measurements were performed by using a CH Instruments, Inc. model CHI 620E electrochemical analyzer. The electrolytic cell used was a conventional two-compartment cell. Electrochemical measurements were performed in dichloromethane solutions with 0.1 M $^{n}Bu_4NPF_6$ as supporting electrolyte at room temperature. The reference electrode was a $Ag/AgNO_3$ (0.1 M in acetonitrile) electrode, and the working electrode was a glassy carbon electrode (CH Instruments, Inc.) with a platinum wire as the counter electrode in a compartment separated from the working electrode by a sintered-glass frit. The ferrocenium/ferrocene couple ($FeCp_2^{+/0}$) was used as the internal reference.[8] All solutions for electrochemical studies were deaerated with pre-purified argon gas

before measurement. Atomic Force Microscopy (AFM) images were obtained using a MFP-3D atomic force microscope (Asylum Research) in tapping mode with a scan rate of 1.0 μm s^{-1}.

Electron Microscopy. Cross-section SEM experiments for the memory devices were performed on a Hitachi S-4800 FEG scanning electron microscope. For the aggregation studies, the SEM experiments were performed either on a Leo 1530 Field-Emission-Gun scanning electron microscope or a Hitachi S-3400N variable pressure scanning electron microscope. All the experiments were conducted at the Electron Microscope Unit of The University of Hong Kong.

Fabrication and Characterization of the Memory Device. The memory devices were fabricated on an indium–tin oxide (ITO)-coated glass substrate which was pre-cleaned by sonicating successively with deionized water, acetone, isopropanol and absolute ethanol for 15 minutes each. A chloroform solution of the gold(I) complex (10 mg ml^{-1}) was spin-coated onto the ITO glass substrate. The thin film was baked on a hot plate at 70 °C for 10 min. Aluminum top electrodes were thermally evaporated and deposited onto the films through a shadow mask at a pressure of *ca.* 5×10^{-6} mbar. Devices with area of *ca.* 0.25 mm^2 were obtained. The devices were characterized under ambient conditions, in a probe station equipped with a Keithley 4200-SCS semiconductor characterization system.

Synthesis and Characterization

General experimental procedure for *N*-alkyloxindole

N-Butyloxindole, *N*-decyloxindole and *N*-tetradecyloxindole were synthesized according to modification of the literature procedure reported for the synthesis of *N*-dodecyloxindole,[1] except that 1-iodobutane (7.6 g, 41.3 mmol), 1-iododecane (11.1 g, 41.3 mmol), or 1-bromotetradecane (11.5 g, 41.3 mmol) was used in place of 1-bromododecane.

***N*-Butyloxindole.** Yield: 2.5 g (35 %). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 0.96 (t, J = 7.4 Hz, 3H, -CH_3), 1.34–1.46 (m , 2H, -CH_2-), 1.61–1.71 (m, 2H, -CH_2-), 3.52 (s, 2H, -CH_2-), 3.71 (t, J = 7.4 Hz, 2H, -NCH_2-), 6.83 (d, J = 7.8 Hz, 1H, phenyl), 7.02 (t, J = 7.5 Hz, 1H, phenyl), 7.21–7.30 (m, 2H, phenyl). HRMS (Positive EI): *m/z* 189.1146 ($[M]^+$).

***N*-Decyloxindole.** Yield: 4.1 g (40 %). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 0.87 (t, J = 6.8 Hz, 3H, -CH_3), 1.17–1.40 (m, 14H, -CH_2-), 1.61–1.71 (m, 2H, -CH_2-), 3.51 (s, 2H, -CH_2-), 3.69 (t, J = 7.4 Hz, 2H, -NCH_2-), 6.83 (d, J = 7.8 Hz, 1H, phenyl), 7.02 (t, J = 7.5 Hz, 1H, phenyl), 7.21–7.30 (m, 2H, phenyl). HRMS (Positive EI): *m/z* 273.2084 ($[M]^+$).

***N*-Tetradecyloxindole.** Yield: 3.8 g (31 %). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 0.88 (t, J = 6.9 Hz, 3H, -CH_3), 1.22–1.41 (m, 22H, -CH_2-), 1.61–1.72 (m, 2H, -CH_2-), 3.52 (s, 2H, -CH_2-), 3.69 (t, J = 7.4 Hz, 2H, -NCH_2-), 6.83 (d, J = 7.8 Hz, 1H, phenyl), 7.03 (t, J = 7.5 Hz, 1H, phenyl), 7.22–7.30 (m, 2H, phenyl). HRMS (Positive EI): *m/z*

329.2709 ($[M]^+$).

General experimental procedure for 5-bromo-*N*-alkyloxindole

They were synthesized according to modification of a literature procedure reported for the synthesis of 5-bromo-*N*-ethyloxindole,[9] except that *N*-butyloxindole (2.5 g, 13.3 mmol), *N*-decyloxindole (3.6 g, 13.3 mmol), *N*-dodecyloxindole (4.0 g, 13.3 mmol) or *N*-tetradecyloxindole (4.4 g, 13.3 mmol) was used in place of *N*-ethyloxindole.

5-Bromo-*N*-butyloxindole. Yield: 3.1 g (88 %). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 0.95 (t, J = 7.3 Hz, 3H, -CH_3), 1.31–1.45 (m, 2H, -CH_2-), 1.57–1.69 (m, 2H, -CH_2-), 3.51 (s, 2H, -CH_2-), 3.68 (t, J = 7.3 Hz, 2H, -NCH_2-), 6.70 (d, J = 8.5 Hz, 1H, phenyl), 7.37 (s, 1H, phenyl), 7.39 (d, J = 8.5 Hz, 1H, phenyl). HRMS (Positive EI): *m/z* 267.0250 ($[M]^+$).

5-Bromo-*N*-decyloxindole. Yield: 4.4 g (94 %). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 0.88 (t, J = 6.8 Hz, 3H, -CH_3), 1.13–1.41 (m, 14H, -CH_2-), 1.61–1.70 (m, 2H, -CH_2-), 3.51 (s, 2H, -CH_2-), 3.67 (t, J = 7.4 Hz, 2H, -NCH_2-), 6.70 (d, J = 8.5 Hz, 1H, phenyl), 7.37 (s, 1H, phenyl), 7.39 (d, J = 8.5 Hz, 1H, phenyl). HRMS (Positive EI): *m/z* 351.1189 ($[M]^+$).

5-Bromo-*N*-dodecyloxindole. Yield: 4.8 g (95 %). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 0.88 (t, J = 6.7 Hz, 3H, -CH_3), 1.16–1.42 (m, 18H, -CH_2-), 1.59–1.71 (m, 2H, -CH_2-), 3.51 (s, 2H, -CH_2-), 3.67 (t, J = 7.4 Hz, 2H, -NCH_2-), 6.70 (d, J = 8.4 Hz, 1H, phenyl), 7.37 (s, 1H, phenyl), 7.39 (d, J = 8.4 Hz, 1H, phenyl). HRMS (Positive EI):

m/z 379.1498 ($[M]^+$).

5-Bromo-*N*-tetradecyloxindole. Yield: 4.8 g (89 %). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 0.88 (t, J = 6.7 Hz, 3H, -CH_3), 1.20–1.38 (m, 22H, -CH_2-), 1.59–1.72 (m, 2H, -CH_2-), 3.51 (s, 2H, -CH_2-), 3.67 (t, J = 7.4 Hz, 2H, -NCH_2-), 6.70 (d, J = 8.1 Hz, 1H, phenyl), 7.34–7.43 (m, 2H, phenyl). HRMS (Positive EI): *m/z* 407.1816 ($[M]^+$).

General experimental procedure for 3,8,13-tribromo-5,10,15-trialkyltriindole

They were synthesized according to modification of a literature procedure reported for the synthesis of 3,8,13-tribromo-5,10,15-triethyltriindole,[9] except that 5-bromo-*N*-butyloxindole (3.2 g, 11.9 mmol), 5-bromo-*N*-decyloxindole (4.2 g, 11.9 mmol), 5-bromo-*N*-dodecyloxindole (4.5 g, 11.9 mmol) or 5-bromo-*N*-tetradecyloxindole (4.9 g, 11.9 mmol) was used in place of 5-bromo-*N*-ethyloxindole.

3,8,13-Tribromo-5,10,15-tributyltriindole. Yield: 0.31 g (10 %). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 0.93 (t, J = 7.3 Hz, 9H, -CH_3), 1.26–1.34 (m, 6H, -CH_2-), 1.84–2.05 (m, 6H, -CH_2-), 4.62 (t, J = 7.9 Hz, 6H, -NCH_2-), 7.43 (d, J = 8.6 Hz, 3H, phenyl), 7.52 (d, J = 8.6 Hz, 3H, phenyl), 8.22 (s, 3H, phenyl). HRMS (Positive EI): *m/z* 747.0449 ($[M]^+$).

3,8,13-Tribromo-5,10,15-tridecyltriindole. Yield: 0.76 g (19 %). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 0.86 (t, J = 6.9 Hz, 9H, -CH_3), 1.10–1.42 (m, 42H, -CH_2-), 1.90–2.06 (m, 6H, -CH_2-), 4.64 (t, J = 7.9 Hz, 6H, -NCH_2-), 7.43 (d, J = 8.6 Hz, 3H, phenyl), 7.52 (d, J = 8.6 Hz, 3H, phenyl), 8.24 (s, 3H, phenyl). HRMS (Positive ESI): *m/z* 999.3257 ($[M]^+$).

3,8,13-Tribromo-5,10,15-tridodecyltriindole. Yield: 0.91 g (21 %). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 0.87 (t, J = 6.8 Hz, 9H, -CH_3), 1.12–1.43 (m, 54H, -CH_2-), 1.94–2.09 (m, 6H, , -CH_2-), 4.74 (t, J = 8.0 Hz, 6H, -NCH_2-), 7.47 (d, J = 8.6 Hz, 3H, phenyl), 7.53 (d, J = 8.6 Hz, 3H, phenyl), 8.31 (s, 3H, phenyl). HRMS (Positive ESI): *m/z* 1083.4189 ($[M]^+$).

3,8,13-Tribromo-5,10,15-tritetradecyltriindole. Yield: 0.98 g (21 %). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 0.88 (t, J = 6.8 Hz, 9H, -CH_3), 1.15–1.42 (m, 66H, -CH_2-), 1.93–2.10 (m, 6H, -CH_2-), 4.73 (t, J = 7.9 Hz, 6H, -NCH_2-), 7.47 (d, J = 8.7 Hz, 3H, phenyl), 7.53 (d, J = 8.7 Hz, 3H, phenyl), 8.31 (s, 3H, phenyl). HRMS (Positive ESI): *m/z* 1167.5117 ($[M]^+$).

General experimental procedure for 3,8,13-tris(trimethylsilylethynyl)-5,10,15-trialkyltriindole

They were synthesized according to modification of a literature procedure reported for the synthesis of 3,8,13-tris(trimethylsilylethynyl)-5,10,15-triethyltriindole,[9] except that 3,8,13-tribromo-5,10,15-tributyltriindole (0.20 g, 0.27 mmol), 3,8,13-tribromo-5,10,15-tridecyltriindole (0.27 g, 0.27 mmol), 3,8,13-tribromo-5,10,15-tridodecyltriindole (0.29 g, 0.27 mmol) or 3,8,13-tribromo-5,10,15-tritetradecyltriindole (0.32 g, 0.27 mmol) was used in place of 3,8,13-tribromo-5,10,15-triethyltriindole.

3,8,13-Tris(trimethylsilylethynyl)-5,10,15-tributyltriindole. Yield: 0.14 g (66 %). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 0.32 (s, 27H, -$SiMe_3$), 0.98 (t, J = 7.4 Hz, 9H, -CH_3), 1.38–1.50 (m, 6H, -CH_2-), 2.00–2.17 (m, 6H, -CH_2-), 4.80 (t, J = 8.0 Hz,

6H, -NCH_2-), 7.52 (d, J = 8.5 Hz, 3H, phenyl), 7.57 (d, J = 8.5 Hz, 3H, phenyl), 8.34 (s, 3H, phenyl). HRMS (Positive EI): *m/z* 801.4306 ($[M]^+$).

3,8,13-Tris(trimethylsilylethynyl)-5,10,15-tridecyltriindole. Yield: 0.25 g (89 %). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 0.31 (s, 27H, -$SiMe_3$), 0.85 (t, J = 7.0 Hz, 9H, -CH_3), 1.09–1.42 (m, 42H, -CH_2-), 1.93–2.13 (m, 6H, -CH_2-), 4.86 (t, J = 7.9 Hz, 6H, -NCH_2-), 7.53 (d, J = 8.5 Hz, 3H, phenyl), 7.58 (d, J = 8.5 Hz, 3H, phenyl), 8.37 (s, 3H, phenyl). HRMS (Positive ESI): *m/z* 1053.7127 ($[M]^+$).

3,8,13-Tris(trimethylsilylethynyl)-5,10,15-tridodecyltriindole. Yield: 0.24 g (78 %). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 0.31 (s, 27H, -$SiMe_3$), 0.87 (t, J = 7.0 Hz, 9H, -CH_3), 1.09–1.45 (m, 54H, -CH_2-), 1.95–2.11 (m, 6H, -CH_2-), 4.84 (t, J = 7.8 Hz, 6H, -NCH_2-), 7.52 (d, J = 8.9 Hz, 3H, phenyl), 7.57 (d, J = 8.9 Hz, 3H, phenyl), 8.36 (s, 3H, phenyl). HRMS (Positive ESI): *m/z* 1137.8050 ($[M]^+$).

3,8,13-Tris(trimethylsilylethynyl)-5,10,15-tritetradecyltriindole. Yield: 0.32 g (97 %). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 0.31 (s, 27H, -$SiMe_3$), 0.87 (t, J = 6.7 Hz, 9H, -CH_3), 1.05–1.48 (m, 66H, -CH_2-), 1.94–2.15 (m, 6H, -CH_2-), 4.85 (t, J = 7.7 Hz, 6H, -NCH_2-), 7.52 (d, J = 8.5 Hz, 3H, phenyl), 7.58 (d, J = 8.5 Hz, 3H, phenyl), 8.36 (s, 3H, phenyl). HRMS (Positive ESI): *m/z* 1221.8986 ($[M]^+$).

General experimental procedure for 3,8,13-triethynyl-5,10,15-trialkyltriindole

They were synthesized according to modification of a literature procedure reported for the synthesis of 3,8,13-triethynyl-5,10,15-triethyltriindole,[9] except that 3,8,13-tris(trimethylsilylethynyl)-5,10,15-tributyltriindole (0.11 g, 0.14 mmol),

3,8,13-tris(trimethylsilylethynyl)-5,10,15-tridecyltriindole (0.15 g, 0.14 mmol), 3,8,13-tris(trimethylsilylethynyl)-5,10,15-tridodecyltriindole (0.16 g, 0.14 mmol) or 3,8,13-tris(trimethylsilylethynyl)-5,10,15-tritetradecyltriindole (0.17 g, 0.14 mmol) was used in place of 3,8,13-tris(trimethylsilylethynyl)-5,10,15-triethyltriindole.

3,8,13-Triethynyl-5,10,15-tributyltriindole. Yield: 58 mg (70 %). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 0.93 (t, J = 7.3 Hz, 9H, -CH_3), 1.31–1.46 (m, 6H, -CH_2-), 1.92–2.13 (m, 6H, -CH_2-), 3.11 (s, 3H, -C≡C-H), 4.83 (t, J = 7.8 Hz, 6H, -NCH_2-), 7.55 (d, J = 8.4 Hz, 3H, phenyl), 7.60 (d, J = 8.4 Hz, 3H, phenyl), 8.40 (s, 3H, phenyl). HRMS (Positive EI): *m/z* 585.3112 ($[M]^+$).

3,8,13-Triethynyl-5,10,15-tridecyltriindole. Yield: 95 mg (81 %). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 0.86 (t, J = 5.6 Hz, 9H, -CH_3), 1.05–1.40 (m, 42H, -CH_2-), 1.79–2.09 (m, 6H, -CH_2-), 3.10 (s, 3H, -C≡C-H), 4.65 (t, J = 7.8 Hz, 6H, -NCH_2-), 7.47 (d, J = 8.2 Hz, 3H, phenyl), 7.56 (d, J = 8.2 Hz, 3H, phenyl), 8.29 (s, 3H, phenyl). HRMS (Positive EI): *m/z* 837.5903 ($[M]^+$).

3,8,13-Triethynyl-5,10,15-tridodecyltriindole. Yield: 102 mg (79 %). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 0.87 (t, J = 6.9 Hz, 9H, -CH_3), 1.11–1.41 (m, 54H, -CH_2-), 1.90–2.07 (m, 6H, -CH_2-), 3.10 (s, 3H, -C≡C-H), 4.70 (t, J = 7.9 Hz, 6H, -NCH_2-), 7.49 (d, J = 8.4 Hz, 3H, phenyl), 7.57 (d, J = 8.4 Hz, 3H, phenyl), 8.31 (s, 3H, phenyl). HRMS (Positive EI): *m/z* 921.6890 ($[M]^+$).

3,8,13-Triethynyl-5,10,15-tritetradecyltriindole. Yield: 101 mg (72 %). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 0.87 (t, J = 6.7 Hz, 9H, -CH_3), 1.12–1.42 (m, 66H,

-CH_2-), 1.90–2.09 (m, 6H, -CH_2-), 3.10 (s, 3H, -C≡C-H), 4.69 (t, J = 7.8 Hz, 6H, -NCH_2-), 7.49 (d, J = 8.5 Hz, 3H, phenyl), 7.57 (d, J = 8.5 Hz, 3H, phenyl), 8.31 (s, 3H, phenyl). HRMS (Positive ESI): *m/z* 1005.7802 ($[M]^+$).

General experimental procedure for [{trialkyltriindole-(C≡C)$_3$}Au$_3$]$_\infty$

The alkynylgold(I) polymers were prepared according to modification of a literature procedure.[10] [Au(tht)Cl] (118 mg, 0.37 mmol) was added to a mixture of the corresponding 3,8,13-triethynyl-5,10,15-trialkyltriindole (0.13 mmol) and NaOAc (302 mg, 3.68 mmol) in THF–MeOH (1:1 v/v, 30 ml). The mixture was stirred in the dark under nitrogen for 1 hr. The yellow precipitate was filtered, washed with water and methanol, and dried under vacuum. ***Caution:*** *The alkynylgold(I) polymer is potentially explosive and should be handled with great caution.*

[1,3-Bis(4-methoxybenzyl)imidazol-2-ylidene]gold(I) chloride. To a solution of 1,3-bis(4-methoxybenzyl)imidazolium bromide (252 mg, 0.647 mmol) in degassed dichloromethane (25 ml) was added silver(I) oxide (75 mg, 0.324 mmol). The mixture was stirred under nitrogen for 6 hr at 40 °C. After the mixture was cooled to room temperature, [Au(tht)Cl] (208 mg, 0.647 mmol) was added and the mixture was stirred overnight at room temperature. The solution was filtered and evaporated to dryness under reduced pressure. The crude product was then purified by flash column chromatography on neutral alumina using chloroform as eluent. Recrystallization by layering hexane onto a concentrated dichloromethane solution yielded the product as colourless crystals. Yield: 259 mg (74 %). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 3.80 (s, 6H, -OCH_3), 5.31 (s, 4H, -CH_2-), 6.81 (s, 2H, imidazolyl of NHC), 6.88 (d, J = 8.5 Hz, 4H, phenyl), 7.28 (d, J = 8.5 Hz, 4H, phenyl). HRMS (Positive ESI): *m/z*

563.0763 ([M+Na]$^+$).

General experimental procedure for complexes 1–4

To a solution of the corresponding [{trialkyltriindole-(C≡C)$_3$}Au$_3$]$_\infty$ (0.088 mmol) in degassed dichloromethane (15 ml) was added 2,6-dimethoxyphenyl isocyanide (0.26 mmol). The reaction mixture was stirred in the dark under nitrogen for 2 hr. The solution was filtered and concentrated under reduced pressure. Subsequent recrystallization by layering hexane onto concentrated dichloromethane solution or by slow diffusion of diethyl ether vapor into concentrated dichloromethane solution yielded the respective complexes as yellow solids.

[Tributyltriindole{(C≡C)Au(C≡NC$_6$H$_3$(OMe)$_2$-2,6)}$_3$] (1). Yield: 60 mg (41 %). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 0.88 (t, J = 7.3 Hz, 9H, -CH_3), 1.23–1.35 (m, 6H, -CH_2-), 1.86–2.04 (m, 6H, -CH_2-), 3.95 (s, 18H, -OCH_3), 4.90 (t, J = 7.5 Hz, 6H, -NCH_2-), 6.58 (d, J = 8.6 Hz, 6H, phenyl of isocyanide), 7.38 (t, J = 8.6 Hz, 3H, phenyl of isocyanide), 7.50 (d, J = 8.4 Hz, 3H, phenyl of triindole), 7.59 (d, J = 8.4 Hz, 3H, phenyl of triindole), 8.42 (s, 3H, phenyl of triindole). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 300 K): δ 14.04, 19.89, 32.08, 46.95, 56.42, 102.93, 103.71, 103.93, 105.60, 110.15, 115.70, 119.43, 123.03, 126.07, 127.42, 132.27, 139.17, 140.07, 157.09, 163.00. HRMS (Positive ESI): *m/z* 1663.3874 ([M]$^+$). Elemental analysis calcd (%) for $C_{69}H_{63}Au_3N_6O_6$: C, 49.83; H, 3.82; N, 5.05; found: C, 50.01; H, 3.86; N, 5.16.

[Tridecyltriindole{(C≡C)Au(C≡NC$_6$H$_3$(OMe)$_2$-2,6)}$_3$] (2). Yield: 74 mg (44 %). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 0.80 (t, J = 6.6 Hz, 9H, -CH_3), 1.06–1.46 (m, 42H,

-CH_2-), 1.90–2.11 (m, 6H, -CH_2-), 3.94 (s, 18H, -OCH_3), 4.86 (t, J = 7.8 Hz, 6H, -NCH_2-), 6.58 (d, J = 8.6 Hz, 6H, phenyl of isocyanide), 7.38 (t, J = 8.6 Hz, 3H, phenyl of isocyanide), 7.49 (d, J = 8.0 Hz, 3H, phenyl), 7.59 (d, J = 8.0 Hz, 3H, phenyl), 8.42 (s, 3H, phenyl). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$, 300 K): δ 14.13, 22.66, 26.73, 29.41, 29.57, 29.70, 29.79, 30.26, 31.94, 47.17, 56.40, 102.81, 103.70, 105.54, 110.00, 115.69, 119.47, 122.97, 125.99, 127.38, 132.26, 139.10, 140.03, 157.10, 163.03. HRMS (Positive ESI): *m/z* 1915.6628 ($[M]^+$). Elemental analysis calcd (%) for $C_{87}H_{99}Au_3N_6O_6 \bullet C_6H_{14}$: C, 55.80; H, 5.69; N, 4.20; found: C, 55.76; H, 5.43; N, 4.31.

[Tridodecyltriindole{(C≡C)Au(C≡NC_6H_3(OMe)$_2$-2,6)}$_3$] (3). Yield: 79 mg (45 %). ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 0.82 (t, J = 6.9 Hz, 9H, -CH_3), 1.09–1.43 (m, 54H, -CH_2-), 1.88–2.08 (m, 6H, -CH_2-), 3.95 (s, 18H, -OCH_3), 4.86 (t, J = 7.6 Hz, 6H, -NCH_2-), 6.59 (d, J = 8.6 Hz, 6H, phenyl of isocyanide), 7.38 (t, J = 8.6 Hz, 3H, phenyl of isocyanide), 7.49 (d, J = 8.4 Hz, 3H, phenyl), 7.59 (d, J = 8.4 Hz, 3H, phenyl), 8.42 (s, 3H, phenyl). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$, 300 K): δ 14.57, 23.12, 27.17, 29.82, 30.02, 30.15, 30.20, 30.21, 30.26, 30.70, 32.36, 47.59, 56.83, 103.23, 104.13, 104.21, 105.96, 110.42, 116.07, 119.84, 123.40, 126.44, 127.78, 132.67, 139.53, 140.46, 157.54, 163.49. HRMS (Positive ESI): *m/z* 1999.7541 ($[M]^+$). Elemental analysis calcd (%) for $C_{93}H_{111}Au_3N_6O_6 \bullet Et_2O$: C, 56.18; H, 5.88; N, 4.05; found: C, 56.24; H, 5.65; N, 4.28.

[Tritetradecyltriindole{(C≡C)Au(C≡NC_6H_3(OMe)$_2$-2,6)}$_3$] (4). Yield: 86 mg (47 %). ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 0.85 (t, J = 6.9 Hz, 9H, -CH_3), 1.12–1.40 (m, 66H, -CH_2-), 1.94–2.07 (m, 6H, -CH_2-), 3.95 (s, 18H, -OCH_3), 4.86 (t, J = 7.6 Hz,

6H, -NCH_2-), 6.59 (d, J = 8.6 Hz, 6H, phenyl of isocyanide), 7.39 (t, J = 8.6 Hz, 3H, phenyl of isocyanide), 7.49 (d, J = 8.5 Hz, 3H, phenyl), 7.58 (d, J = 8.5 Hz, 3H, phenyl), 8.42 (s, 3H, phenyl). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$, 300 K): δ 14.16, 22.70, 26.74, 29.40, 29.60, 29.64, 29.69, 29.74, 29.78, 29.80, 29.84, 30.28, 31.92, 47.17, 56.40, 102.81, 103.70, 103.76, 105.53, 110.00, 115.68, 119.47, 122.97, 126.00, 127.36, 132.25, 139.10, 140.02, 157.10, 163.05. HRMS (Positive ESI): *m/z* 2083.8562 ($[M]^+$). Elemental analysis calcd (%) for $C_{99}H_{123}Au_3N_6O_6$•Et_2O: C, 57.32; H, 6.21; N, 3.89; found: C, 57.45; H, 6.10; N, 4.13.

General experimental procedure for complexes 5 and 6

To a solution of 3,8,13-triethynyl-5,10,15-tridodecyltriindole (0.08 mmol) in degassed THF–MeOH (4:1 v/v, 50 ml) was added NaOH (100 mg). After the solution was stirred under nitrogen at room temperature for 15 min, the corresponding (1,3-dimethylimidazol-2-ylidene)gold(I) chloride or [1,3-bis(4-methoxybenzyl)imidazol-2-ylidene]gold(I) chloride (239 mmol) was added. The solution was stirred overnight at room temperature. Then, the solution was filtered and evaporated to dryness under reduced pressure. The crude product was purified by flash column chromatography on basic alumina using dichloromethane or chloroform as eluent to give a pale yellow oil. Subsequent recrystallization by slow diffusion of pentane vapor into concentrated benzene solution or diethyl ether vapor into concentrated dichloromethane solution yielded the respective complexes as pale yellow solids.

[Tridodecyltriindole{(C≡C)Au(IMe)}$_3$] (**5**) (IMe = 1,3-dimethylimidazol-2-ylidene)**.** Yield: 50 mg (35 %). ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 0.85 (t, J = 7.0 Hz, 9H,

-CH_3), 1.06–1.31 (m, 54H, -CH_2-), 1.85–1.96 (m, 6H, -CH_2-), 3.88 (s, 18H, -CH_3 of NHC), 4.88 (t, J = 7.2 Hz, 6H, -NCH_2-), 6.90 (s, 6H, imidazolyl of NHC), 7.47 (d, J = 8.4 Hz, 3H, phenyl), 7.60 (d, J = 8.4 Hz, 3H, phenyl), 8.42 (s, 3H, phenyl). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$, 300 K): δ 14.16, 22.70, 26.66, 29.37, 29.48, 29.65, 29.68, 29.72, 29.79, 29.94, 31.91, 37.90, 47.09, 103.04, 106.94, 110.01, 116.64, 121.57, 123.14, 124.79, 125.78, 127.35, 139.12, 139.85, 188.48. HRMS (Positive ESI): *m/z* 1798.7802 ($[M]^+$). Elemental analysis calcd (%) for $C_{81}H_{108}Au_3N_9$: C, 54.09; H, 6.05; N, 7.01; found: C, 54.17; H, 6.07; N, 6.89.

[Tridodecyltriindole{(C≡C)Au(IBOMe)}$_3$] (**6**) (IBOMe = 1,3-bis(4-methoxybenzyl)imidazol-2-ylidene)**.** Yield: 101 mg (52 %). ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 0.83 (t, J = 7.1 Hz, 9H, -CH_3), 1.01–1.30 (m, 54H, -CH_2-), 1.81–1.95 (m, 6H, -CH_2-), 3.81 (s, 18H, -OCH_3), 4.89 (t, J = 7.4 Hz, 6H, -NCH_2-), 5.40 (s, 12H, -CH_2-), 6.78 (s, 6H, imidazolyl of NHC), 6.89 (d, J = 8.5 Hz, 12H, phenyl of NHC), 7.33 (d, J = 8.5 Hz, 12H, phenyl of NHC), 7.46 (d, J = 8.4 Hz, 3H, phenyl of triindole), 7.61 (d, J = 8.4 Hz, 3H, phenyl of triindole), 8.43 (s, 3H, phenyl of triindole). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$, 300 K): δ 14.57, 23.11, 27.00, 29.77, 29.82, 29.97, 30.06, 30.09, 30.20, 30.25, 32.32, 47.49, 54.78, 55.73, 103.48, 107.33, 110.45, 114.73, 117.00, 120.79, 123.57, 125.25, 126.21, 127.77, 127.88, 130.14, 139.54, 140.27, 160.14, 187.54. HRMS (Positive ESI): *m/z* 2436.0355 ($[M]^+$). Elemental analysis calcd (%) for $C_{123}H_{144}Au_3N_9O_6$•C_5H_{12}: C, 61.31; H, 6.27; N, 5.03; found: C, 61.36; H, 6.21; N, 5.06.

Photophysical Data

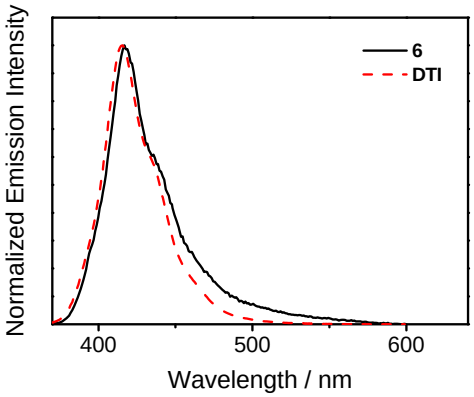

Figure S1. Normalized emission spectra of complex **6** and 3,8,13-tris(trimethylsilylethynyl)-5,10,15-tridodecyltriindole (DTI) in benzene solution under aerobic conditions at 298 K.

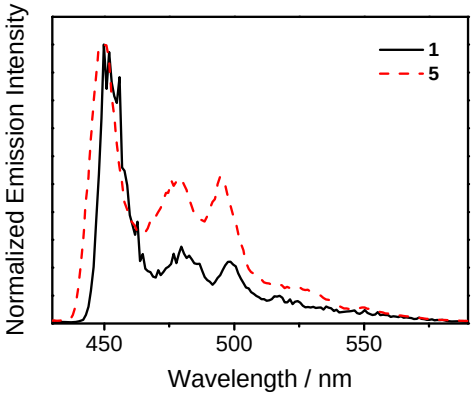

Figure S2. Normalized emission spectra of complexes **1** and **5** in low-temperature butyronitrile glass at 77 K.

Cyclic Voltammetry Data

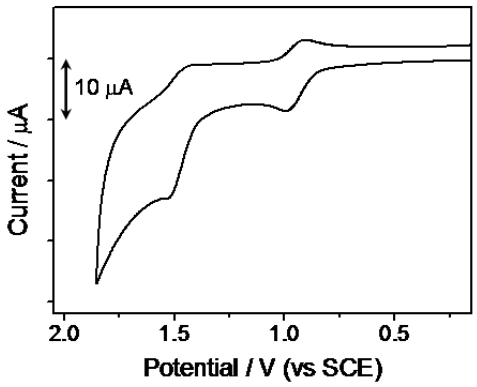

Figure S3. Cyclic voltammogram for the oxidative scan of 3,8,13-triethynyl-5,10,15-tridodecyltriindole in dichloromethane (0.1 M $^{n}Bu_4NPF_6$). Scan rate = 100 mV s^{-1}.

TGA Data

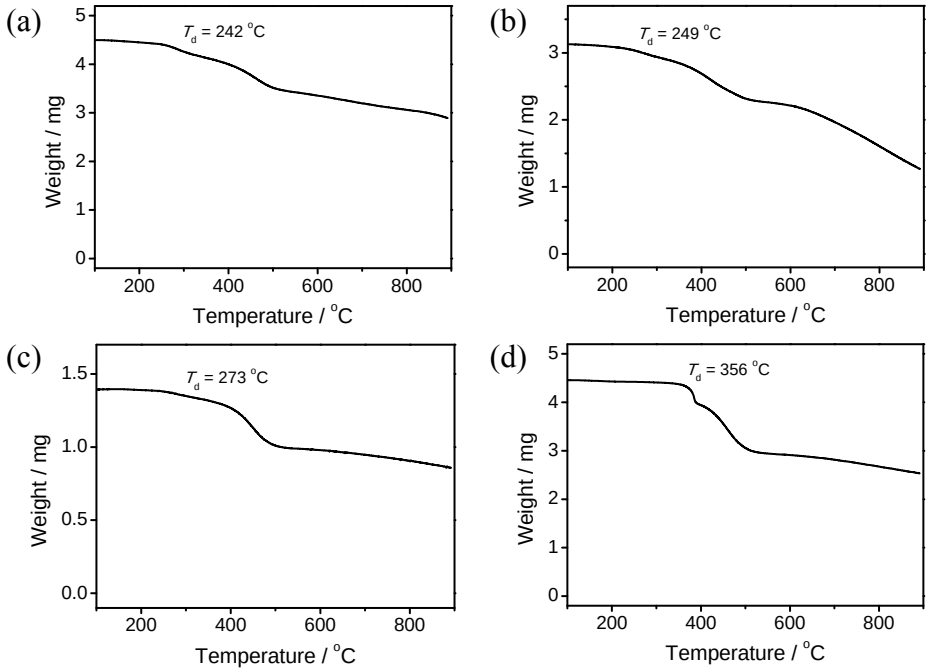

Figure S4. TGA thermograms of (a) **1**, (b) **2**, (c) **3** and (d) **5**. Heating rate = 20 °C min^{-1} under a nitrogen atmosphere. Decomposition temperature (T_d) is defined as the temperature at which the material shows a 5 % weight loss.

Optical Images and AFM Studies

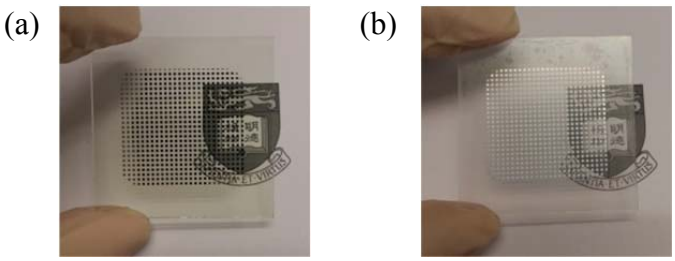

Figure S5. Optical images of the memory devices prepared from (a) complex **4** and (b) 3,8,13-triethynyl-5,10,15-tridodecyltriindole.

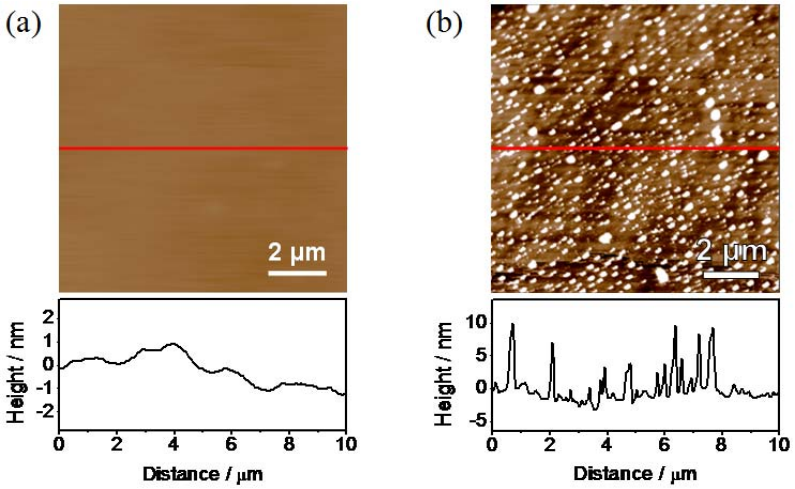

Figure S6. AFM topography and the corresponding height profile of the AFM topographic image of the film prepared from (a) complex **4** and (b) 3,8,13-triethynyl-5,10,15-tridodecyltriindole.

Memory Performances

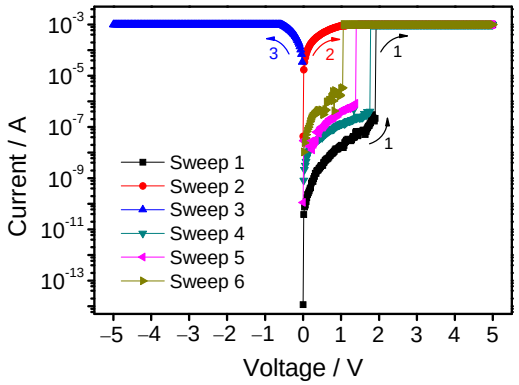

Figure S7. Current–voltage characteristics of the memory devices fabricated with complex **4**. Sweeps 4, 5 and 6 were carried out after turning off the power for 30 minutes repeatedly.

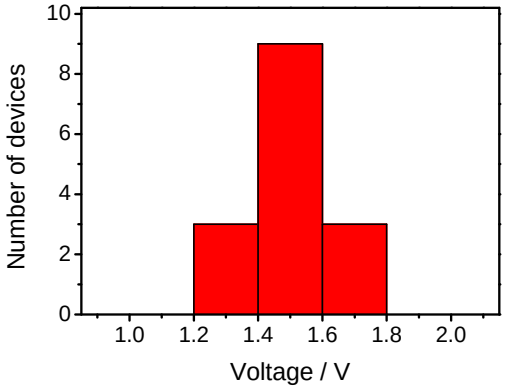

Figure S8. The distribution of the switching threshold voltages (V_{Th}) among 15 memory devices fabricated with complex **4**.

Self-Assembly Studies

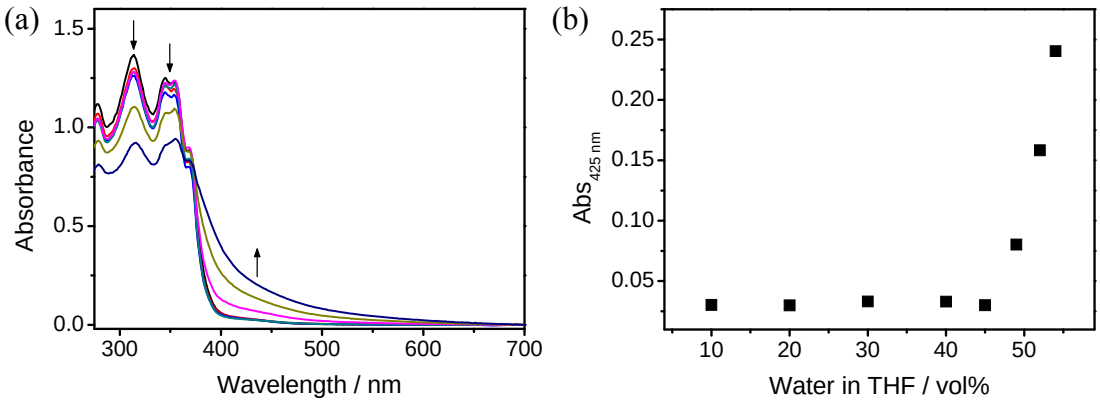

Figure S9. (a) UV-Vis absorption spectral traces of **3** (9.3×10^{-6} M) upon increasing the water content in THF at 298 K. (b) A plot of absorbance at 425 nm as a function of water fraction in THF solution of **3**.

NMR Spectra

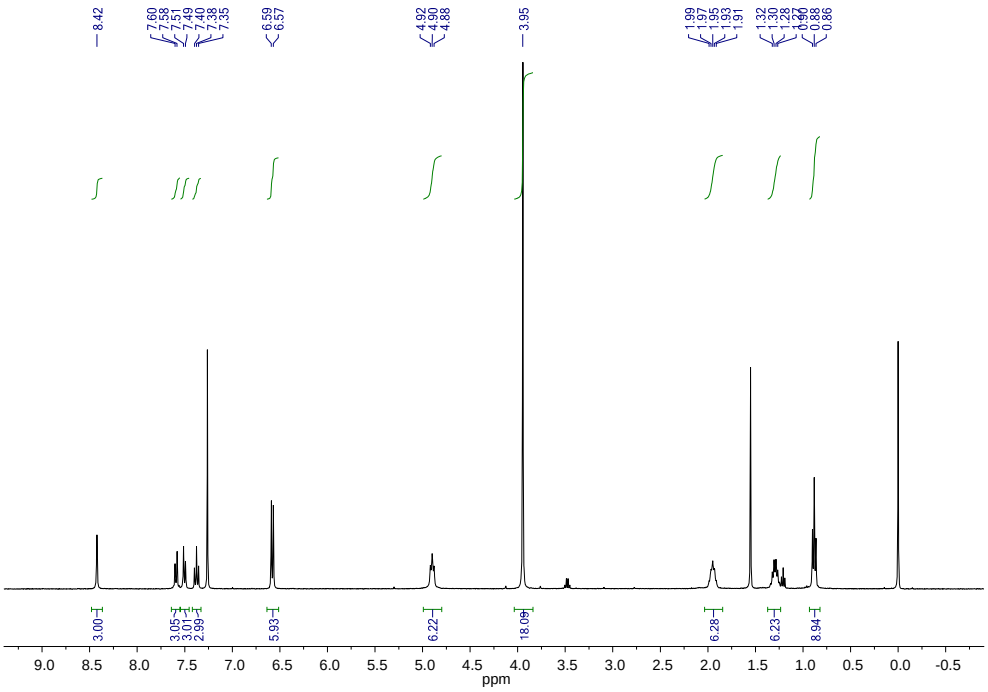

Figure S10. ^{1}H NMR spectrum of complex **1** in $CDCl_3$.

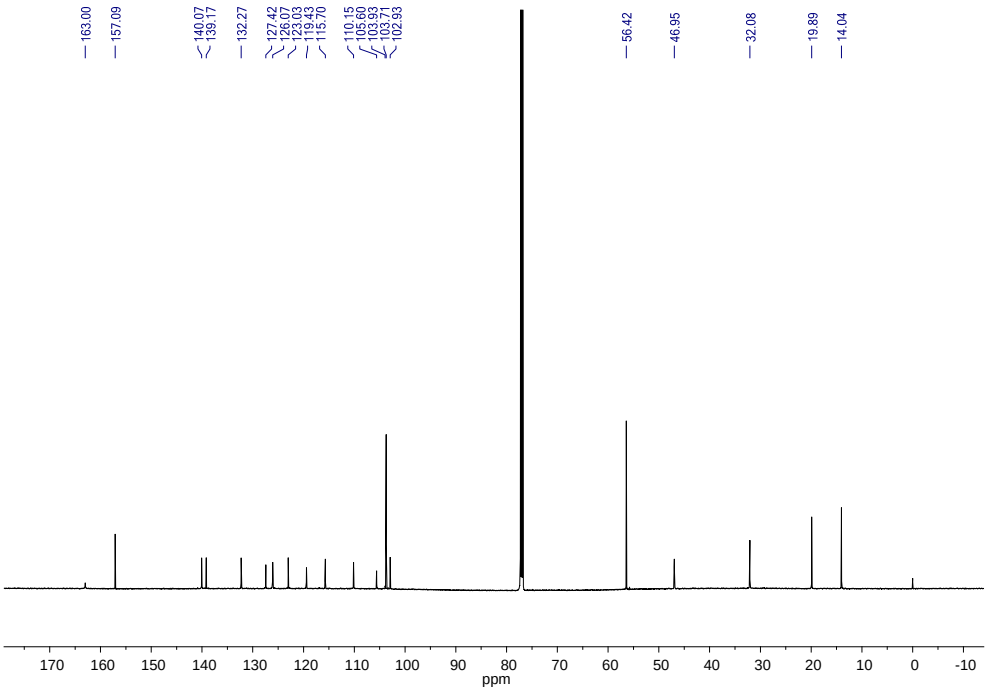

Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum of complex **1** in $CDCl_3$.

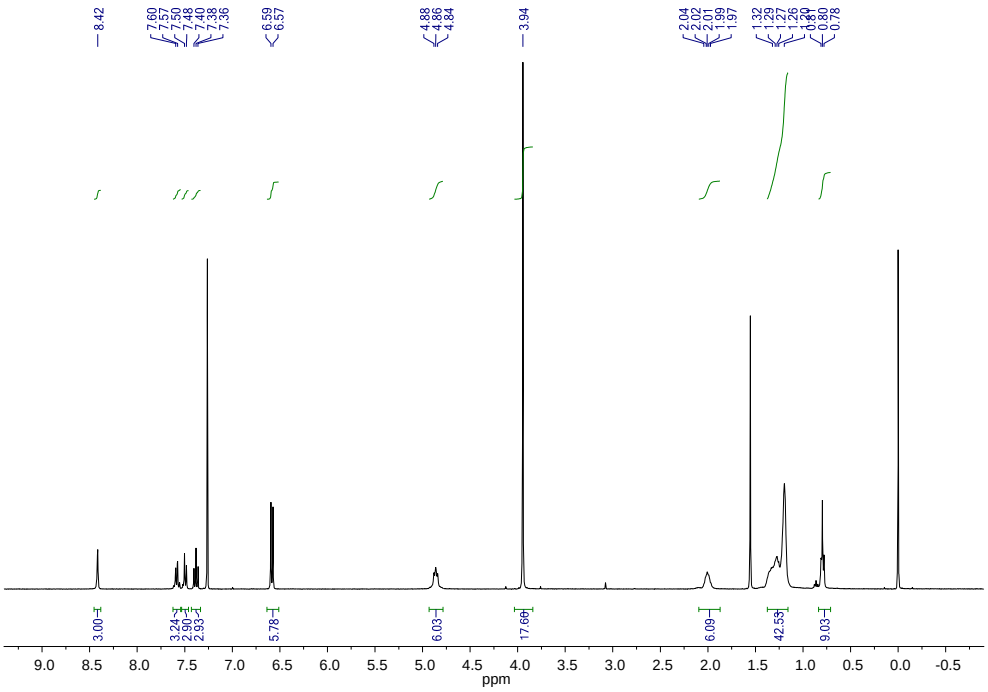

Figure S12. ^{1}H NMR spectrum of complex **2** in $CDCl_3$.

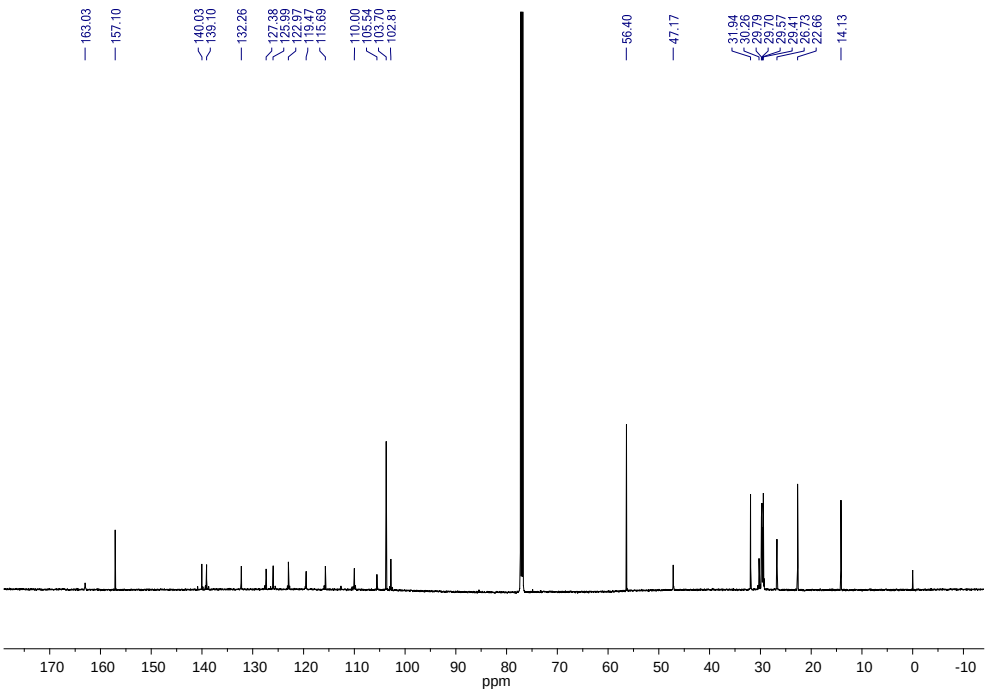

Figure S13. $^{13}C\{^{1}H\}$ NMR spectrum of complex **2** in $CDCl_3$.

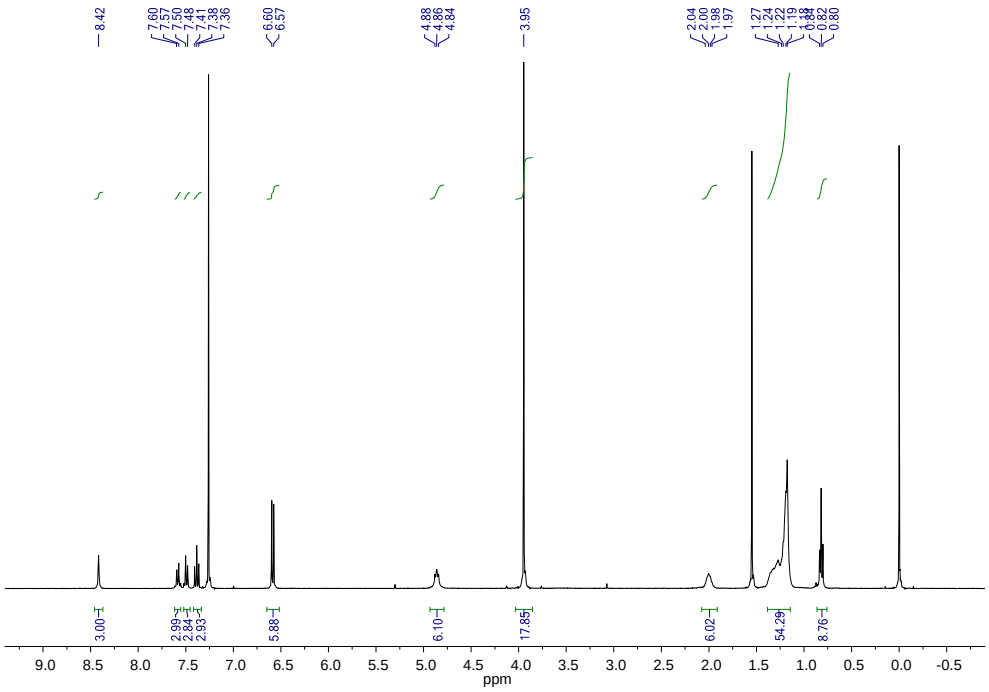

Figure S14. ^{1}H NMR spectrum of complex **3** in $CDCl_3$.

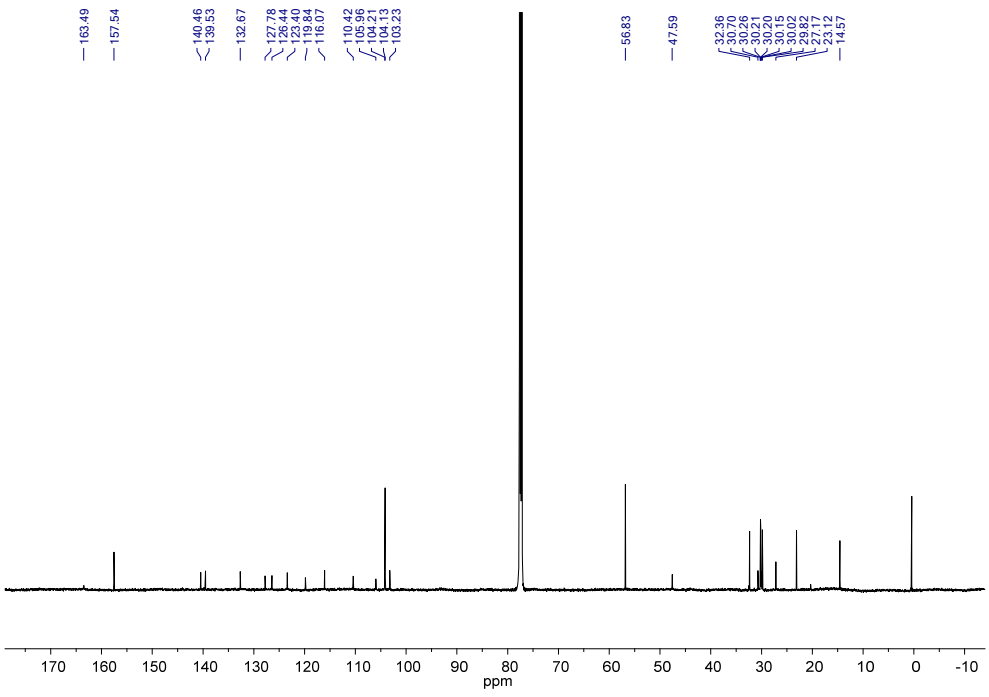

Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum of complex **3** in $CDCl_3$.

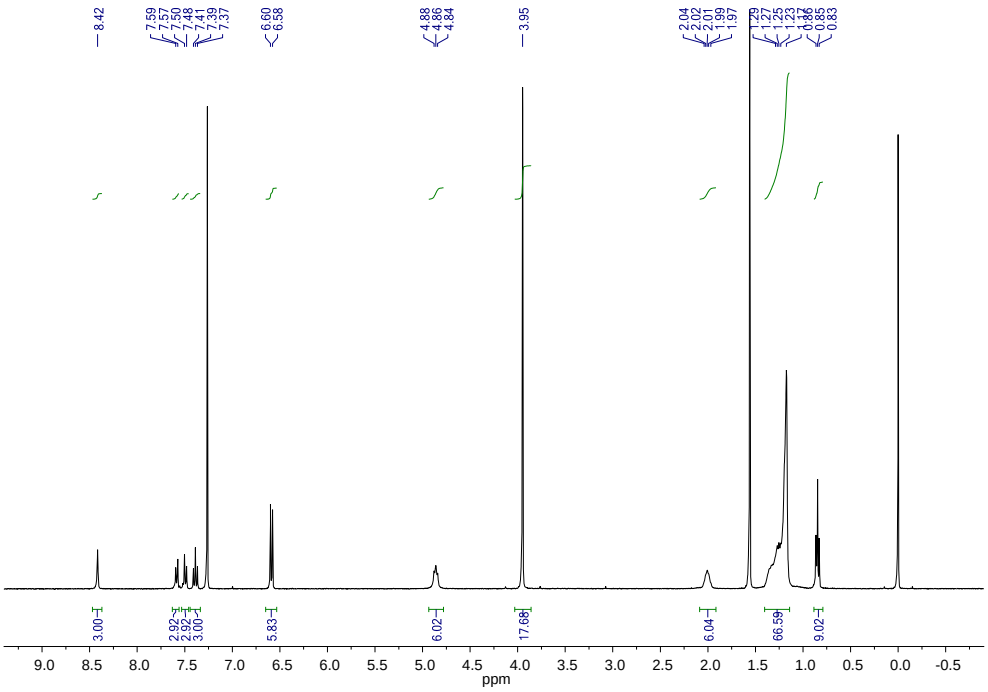

Figure S16. ^{1}H NMR spectrum of complex **4** in $CDCl_3$.

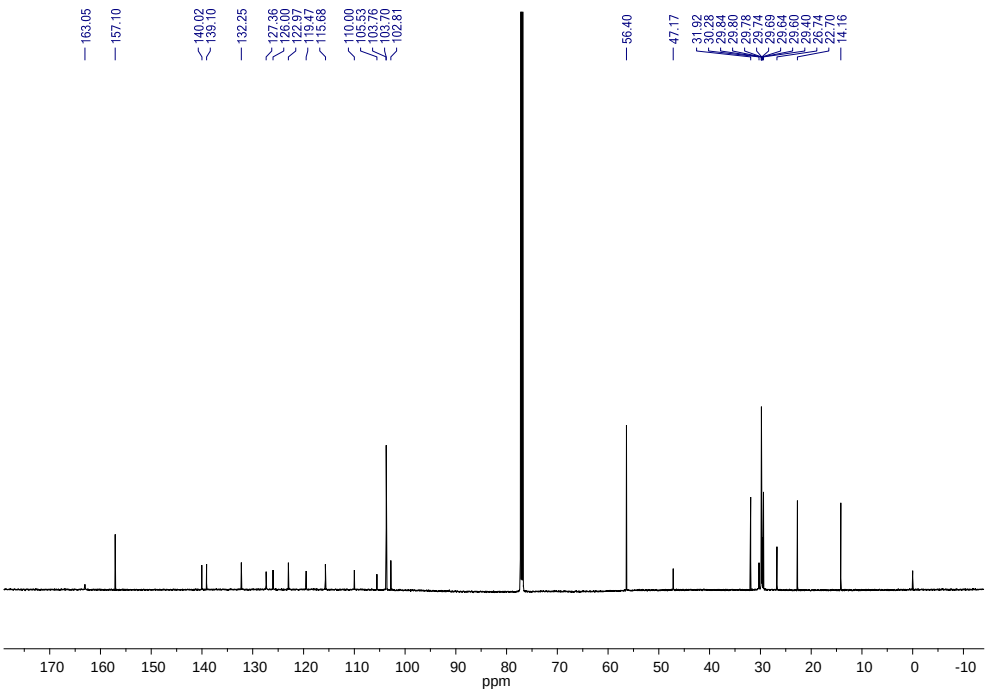

Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum of complex **4** in $CDCl_3$.

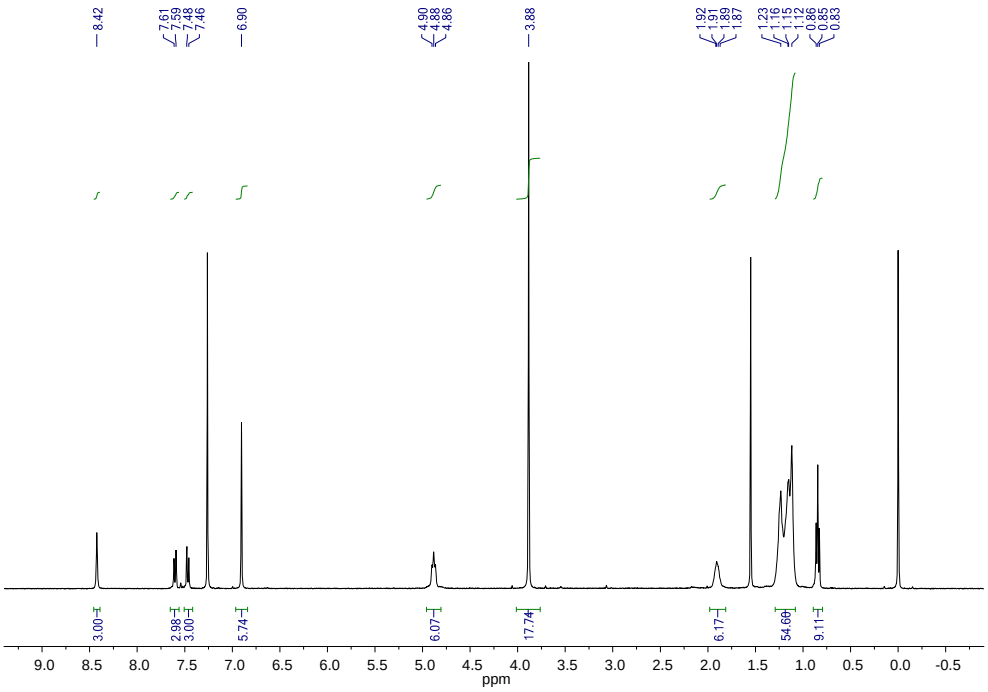

Figure S18. ^{1}H NMR spectrum of complex **5** in $CDCl_3$.

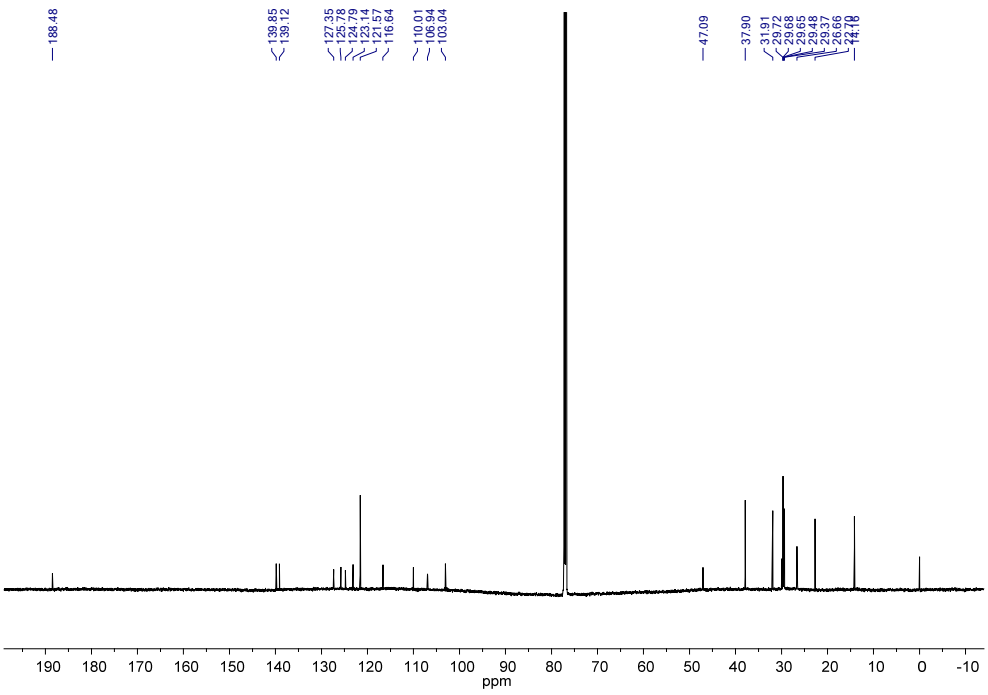

Figure S19. $^{13}C\{^{1}H\}$ NMR spectrum of complex **5** in $CDCl_3$.

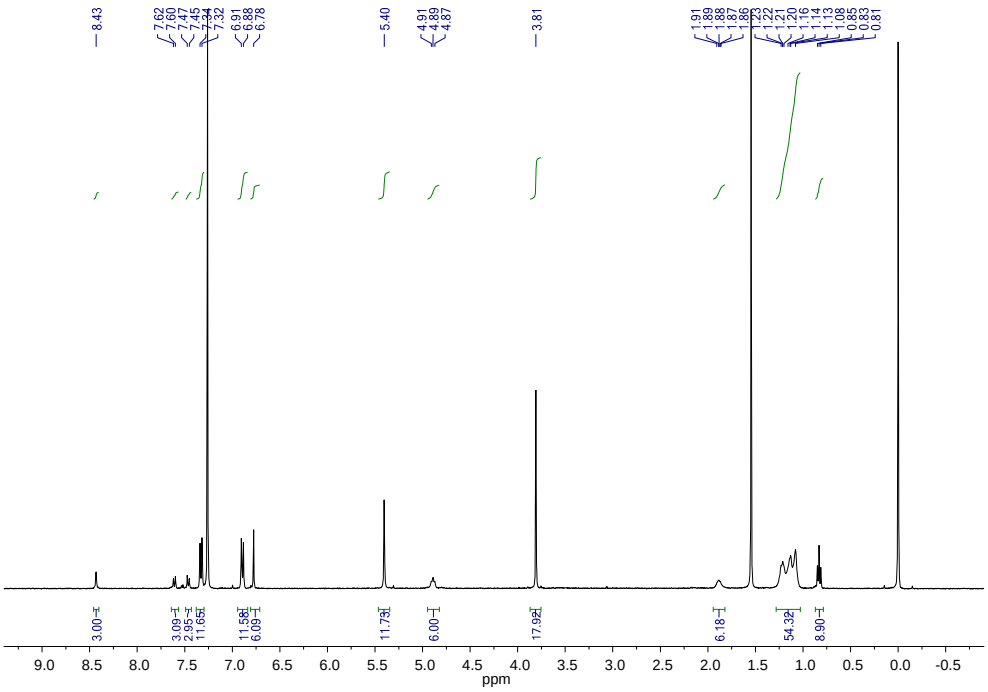

Figure S20. ^{1}H NMR spectrum of complex **6** in $CDCl_3$.

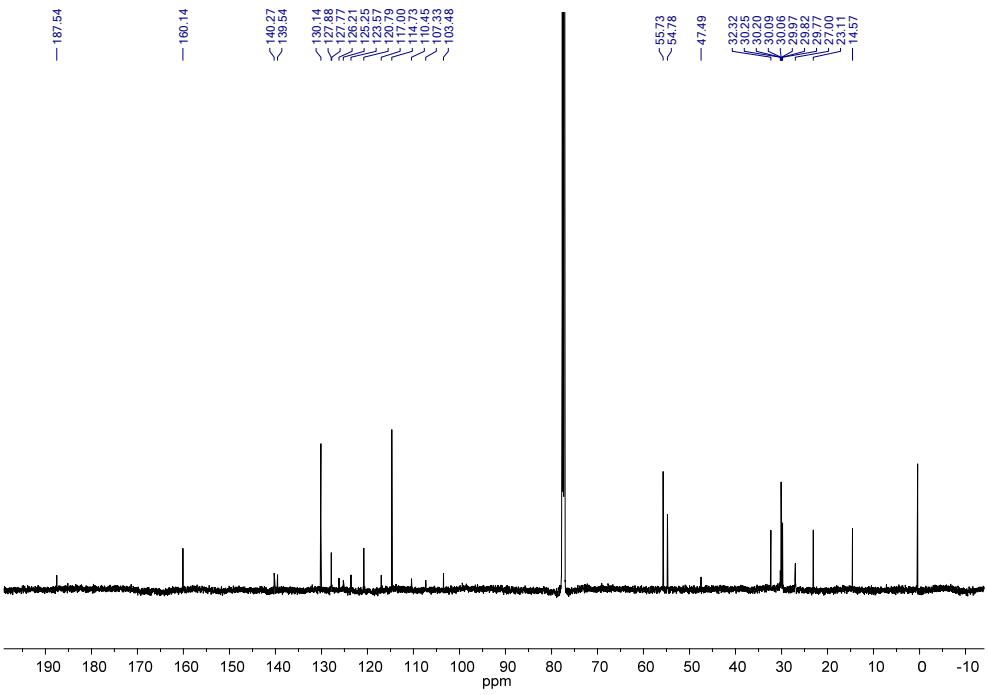

Figure S21. $^{13}C\{^{1}H\}$ NMR spectrum of complex **6** in $CDCl_3$.

References

1 Bura, T.; Leclerc, N.; Fall, S.; Lévêque, P.; Heiser, T.; Ziessel, R. Absorption Tuning of Monosubstituted Triazatruxenes for Bulk Heterojunction Solar Cells. *Org. Lett.* **2011**, *13*, 6030–6033.

2 Uson, R.; Laguna, A; Laguna, M. (Tetrahydrothiophene)Gold(I) or Gold(III) Complexes. *Inorg. Synth.* **1989**, *26*, 85–91.

3 Nieto-Oberhuber, C.; Lopez, S.; Echavarren, A. M. Intramolecular [4 + 2] Cycloadditions of 1,3-Enynes or Arylalkynes with Alkenes with Highly Reactive Cationic Phosphine Au(I) Complexes. *J. Am. Chem. Soc.* **2005**, *127*, 6178–6179.

4 Patil, S.; Claffey, J.; Deally, A.; Hogan, M.; Gleeson, B.; Méndez, L. M. M.; Müller-Bunz, H.; Paradisi, F.; Tacke, M. Synthesis, Cytotoxicity and Antibacterial Studies of *p*-Methoxybenzyl-Substituted and Benzyl-Substituted N-Heterocyclic Carbene–Silver Complexes. *Eur. J. Inorg. Chem.* **2010**, *2010*, 1020–1031.

5 Hashmi, A. S. K.; Yu, Y.; Rominger, F. Efficient One-Pot Synthesis of Unsymmetrical Gold(I) N-Heterocyclic Carbene Complexes and Their Use as Catalysts. *Organomet.* **2012**, *31*, 895–904.

6 Demas, J. N.; Crosby, G. A. The Measurement of Photoluminescence Quantum Yields. A Review. *J. Phys. Chem.* **1971**, *75*, 991–1024.

7 Van Houten, J.; Watts, R. Temperature Dependence of the Photophysical and Photochemical Properties of the Tris(2,2'-bipyridyl)ruthenium(II) Ion in Aqueous Solution. *J. Am. Chem. Soc.* **1976**, *98*, 4853–4858.

8 Connelly, N. G.; Geiger, W. E. Chemical Redox Agents for Organometallic Chemistry. *Chem. Rev.* **1996**, *96*, 877–910.

9 Ji, L.; Fang, Q.; Yuan, M.-S.; Liu, Z.-Q.; Shen, Y.-X.; Chen, H.-F. Switching High Two-Photon Efficiency: From 3,8,13-Substituted Triindole Derivatives to Their 2,7,12-Isomers. *Org. Lett.* **2010**, *12*, 5192–5195.

10 Coates, G. E.; Parkin, C. Gold(I) Alkynyls and their Co-ordination Complexes. *J. Chem. Soc.* **1962**, 3220–3226.