Supporting Information

Au-Involving Chalcogen Bond in 4-(2-Chalcophenyl)-1,2,3-triazolylidene Au(I) Complexes: Synthesis, Characterization and Photophysical Properties

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CONTENTS

I. GENERAL INFORMATION

1. NMR spectra, HR-MS and PXRD characterization

All starting chemicals were purchased from Alfa, Across, Aldrich, TCI, and J&K and used without further purification. Compounds sensitive to air and moisture were operated under Ar or N_2 in the glovebox or standard Schlenk techniques. ^{1}H NMR and ^{13}C NMR spectra were obtained on the Bruker 400 or 600 MHz spectrometer using $CDCl_3$. The chemical shift references were as follows: (^{1}H) $CDCl_3$, 7.26 ppm, (^{13}C) $CDCl_3$, 77.16 ppm. High-resolution mass spectra (HR-MS) were acquired on Thermo (Q-Exactive) instrument using electrospray ionization mode (ESI). Power X-ray diffraction (XRD) patterns of the films were recorded on a Shimadzu XRD-7000 diffractometer using Cu Kα radiation in the 2θ range from 5° to 50° at a scan rate of 2° per min.

2. X-ray crystallographic studies

X-ray diffraction data collections were used on 'Rigaku ST-Saturn724+' and 'Rigaku Synergy-R' diffractometer, Bruker D8 venture Kappa Duo diffractometer equipped with a PHOTON 100 detector, a ImS micro-focus sealed X-ray tube, using graphite-monochromated Mo Kα radiation ((λ = 0.71073 Å) and Cu Kα radiation (λ = 1.54184 Å). All structures were solved by the ShelXT, refined by the SHELXL against F^2 on all data by full-matrix least squares. Established refinement strategies were applied via the OLEX-2 suite of crystallographic programs. All nonhydrogen atoms were refined anisotropically ORTEP drawings using the ORTEP-3 for Windows or Mercury. Carbon bound H atoms were placed in calculated positions and were included in the refinement in the riding model approximation. In all of the structures, the commands RIGU, DELU, SIMU or ISOR were applied to mostly restrain the disorder atoms. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications. CCDC Number: **1**, 2405319. **2**, 2405235. **3**, 2405236. **4**, 2405244. **5**, 2405248. **6**, 2405250. **7**, 2405254. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

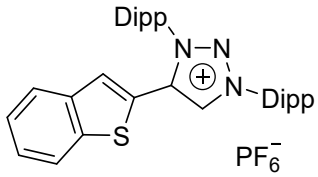
3. Photophysical characterization

Absorption spectra were measured on Agilent Cary 60 UV-Vis spectrophotometer and steady state emission spectra were recorded on Edinburgh spectrofluorometer FS5. Transient PL decays were recorded using Edinburgh fluorescence spectrometer (FLS–980) equipped with 340 nm laser excitation source. Long-lived phosphorescence decays of **2**-**7** at long wavelengths were measured by using a Division of Edinburgh instruments equipped with a μF_2 lamp. Absolute quantum yields at room temperature were measured by an integrating sphere (SM4, Edinburgh Instrument, UK). All the solution was prepared to the quartz cuvettes under Ar in the glovebox.

II. EXPERIMENTS AND RESULTS

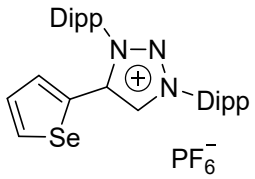
1. Synthesis of compounds

L1-(H^+) was synthesized according to the reported literatures.[1,2]



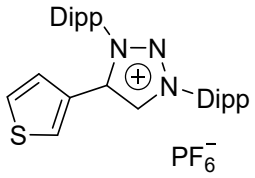
L2-(H^+)

Under N_2 atmosphere, tert-butylhypochlorite (1.36 mL, 12.0 mmol, 1.5 equiv) was added drop by drop to the stirred suspension of 1,3-bis(2,6-diisopropyphenyl)-triazene (2925.0 mg, 8 mmol, 1.0 equiv) and potassium hexafluorophosphate (1914.0 mg, 10.4 mmol, 1.3 equiv) in dry dichloromethane (40.0 mL) at -78 °C. The mixture was stirred for 30 mins. 2-bromovinylbenzo[b]thiophene (2832.0 mg, 12.0 mmol, 1.5 equiv) was added to the mixture under N_2 atmosphere. The resulted mixture was stirred overnight as it was gradually warm to room temperature. The contents were then filtered, and the collected filtrate was were evaporated under reduced pressure. Then the resulted solids were washed with diethyl ether to afford the target product as white powder (3632.3 mg, 68%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.04 (s, 1H), 8.73 (s, 1H), 8.06 (q, *J* = 3.2 Hz, 1H), 7.85 (t, *J* = 7.8 Hz, 1H), 7.70-7.64 (m, 2H), 7.53 (d, *J* = 7.8 Hz, 2H), 7.44-7.39 (m, 4H), 2.46-2.36 (sept, *J* = 6.8 Hz, 2H), 2.34-2.24 (sept, *J* = 6.8 Hz, 2H), 1.40 (d, *J* = 6.8 Hz, 6H), 1.21-1.17 (m, 18H). **^{13}C NMR** (100 MHz, $CDCl_3$): 146.5, 145.1, 142.1, 141.4, 138.5, 134.4, 133.7, 133.4, 131.4, 130.5, 128.7, 126.7, 126.0, 125.7, 125.0, 122.0, 120.0, 29.8, 29.6, 25.2, 24.9, 23.8, 22.9. HRMS (ESI) calcd for: $[C_{34}H_{40}N_3S]^+$, $[M]^+$: *m/z* =522.2937; found 522.2938.



L3-(H^+)

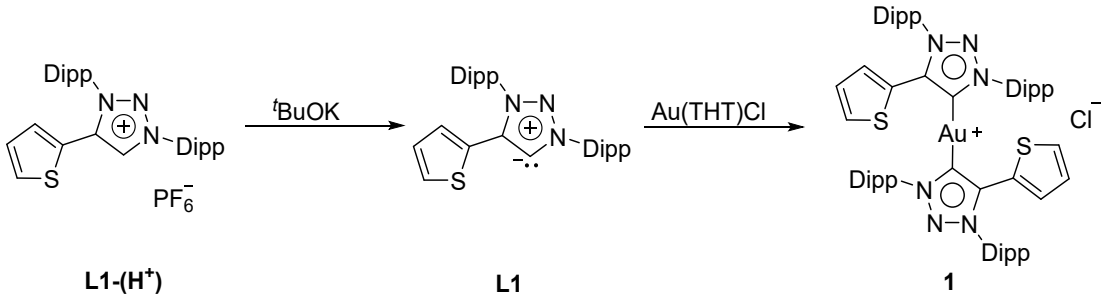
L3-(H^+) was synthesized according to similar procedure as **L2-(H^+)** with2-(2-bromovinyl)selenophene in 62% yield.**^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.61 (s, 1H), 9.51 (d, *J* = 4.0 Hz, 1H), 8.22 (d, *J* = 3.8 Hz, 1H), 7.81 (t, *J* = 7.8 Hz, 1H), 7.66 (t, *J* = 7.9 Hz, 1H), 7.52-7.46 (m, 3H), 7.42 (d, *J* = 7.9 Hz, 2H), 2.40-2.34 (sept, 2H), 2.29-2.22 (sept, 2H), 1.39 (d, *J* = 3.9 Hz, 6H), 1.20-1.16 (m, 18H). **^{13}C NMR** (100 MHz, $CDCl_3$): 146.7, 145.1, 143.6, 139.1, 138.7, 134.4, 133.3, 131.8, 130.6, 129.3, 128.2, 126.0, 125.0, 124.0, 29.7, 29.5, 25.3, 24.9, 23.7, 22.8. HRMS (ESI) calcd for: $[C_{30}H_{38}N_3Se]^+$, $[M]^+$: m/z = 520.2225; found 520.2224.



L4-(H^+)

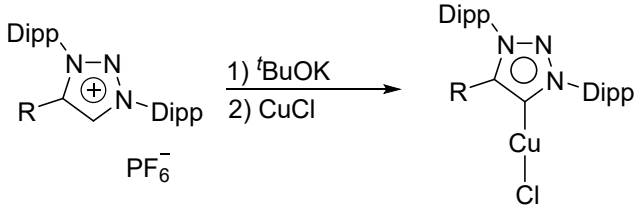
L4-(H^+) was synthesized according to similar procedure as **L1-(H^+)** with 3-ethynylthiophene in 91% yield. **^{1}H NMR** (400 MHz, DMSO-d_6: δ 10.24 (s, 1H), 7.88-7.83 (m, 2H), 7.80 (t, *J* = 7.8 Hz, 1H), 7.67 (d, *J* = 7.8 Hz, 2H), 7.83 (d, *J* = 7.8 Hz, 2H), 7.57 (q, *J* = 1.4 Hz, 1H), 7.11 (dd, *J* = 1.4 , 5.2 Hz, 1H), 2.51-2.42 (sept, *J* = 6.8 Hz, 2H), 2.39-2.29 (sept, *J* = 6.8 Hz, 2H), 1.31 (d, *J* = 6.8 Hz , 6H), 1.12 (d, *J* = 6.9 Hz, 12H), 1.03 (d, *J* = 6.8 Hz , 6H). **^{13}C NMR** (100 MHz, DMSO-d_6): 145.0, 144.9, 140.9, 133.9, 133.3, 132.5, 130.2, 130.0, 129.8, 129.0, 126.0, 125.9, 125.0, 121.8, 28.6, 28.5, 24.4, 24.3, 23.4, 22.3. HRMS (ESI) calcd for $C_{30}H_{38}N_3S^+$, $[M]^+$: *m/z* = 472.2781; found 472.2773.

Compound **1**

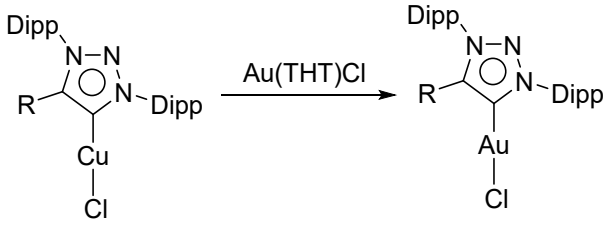


L1-(H^+) **L1** **1**

Under N_2 atmosphere, KO^{t}Bu (0.7 mmol, 78.4 mg, 1.4 equiv) were added to the solution of 1,3-bis(2,6-diisopropyphenyl)-4-(2-thienyl)-1,2,3-triazolium hexafluorophosphate **L1-(H^+)** (0.5 mmol, 308.5 mg, 1.0 equiv) in degassed tetrahydrofuran (5.0 mL) in 25mL Schlenk tube at 0°C. The mixture was stirred for 30 mins. Then the solvents were removed by *vacuo*. The solid residue was extracted with anhydrous toluene under N_2 atmosphere. The filtrate was collected and volatiles were evaporated by vacuo. After that, **L1** was obtained. Under N_2 atmosphere, Au(THT)Cl (0.25 mmol, 80.0 mg, 0.5 equiv) was added into a stirred solution of L1(333.0 mg , 0.5 mmol, 1.0 equiv) in THF (5.0 mL) at room temperature. Then the mixture was stirred for 3 h. After the mixture was filtered, the solvent was removed under reduced pressure. The residue was further purified by column chromatography (CH_2Cl_2: CH_3OH 20:1) and finally the white solid was obtained (275.3 mg,0.19 mmol, 77%). **^{1}H NMR (400** MHz, $CDCl_3$): δ 7.71 (t, *J* = 7.8 Hz, 2H), 7.68 (t, *J* = 7.9 Hz, 2H), 7.41 (d, *J* = 2.0 Hz, 4H), 7.39 (d, *J* = 2.0 Hz, 4H),7.11 (dd, *J* = 1.2 , 5.1 Hz, 2H), 6.73(dd, *J* = 3.8 , 5.0 Hz, 2H), 6.38 (dd, *J* = 1.2 , 3.9 Hz, 2H), 2.43 (sept, *J* = 6.9 Hz, 4H), 2.22 (sept, *J* = 6.9 Hz, 4H), 1.27 (d, *J* = 6.8 Hz, 12H), 1.19 (d, *J* = 6.8 Hz, 12H), 1.14 (d, *J* = 6.8 Hz, 12H), 1.01 (d, J = 6.8 Hz, 12H). 13C NMR (100 MHz, CDCl3): δ 172.4, 145.4, 145.4, 144.7, 135.1, 133.2, 132.2, 130.6, 129.8, 128.3, 128.1, 126.6, 125.4, 124.8, 29.3, 29.2, 24.9, 24.4, 24.1, 22.7. HRMS (ESI): calcd for: $[C_{60}H_{74}AuN_6S_2]^+$ $[M]^+$: m/z = 1139.5076, found: 1139.5046.



R = 2-thienyl	**L1-(H^+)**	**8**
R = 2-benzo[*b*]thienyl	**L2-(H^+)**	**9**
R = 2-selenophenyl	**L3-(H^+)**	**10**
R = 3-thienyl	**L4-(H^+)**	**11**

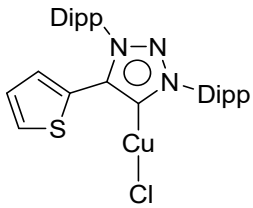


8	**2**
9	**3**
10	**4**
11	**5**

General Procedure for the Preparation of **8-11**

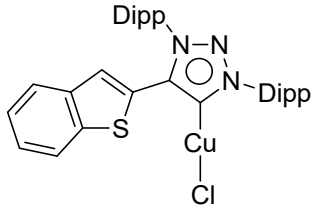
Under argon atmosphere, the mixture of **L1-(H^+)**, **L2-(H^+)**, **L3-(H^+)** or **L4-(H^+)** (0.3 mmol, 1 equiv) and KOBu^t (0.39 mmol, 1.3 equiv) in anhydrous THF (5.0 mL) in 25 mL Schlenk tube was stirred at 0˚C for 30 mins. After that, CuCl (0.45 mmol, 1.5 equiv) was added into the system under argon atmosphere and then the mixture was stirred for 3 hours at room temperature. After the resulting mixture was filtered and filtrate was collected. The volatiles were evaporated under reduced pressure to afford the products **8**, **9**, **10** or **11**.

Complex **8**



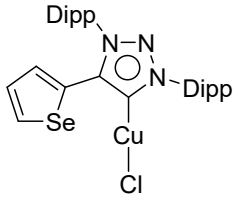
8 was obtained as the light green powder (0.29 mmol, 95%).**^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.67 (t, *J* = 7.8 Hz, 1H), 7.55 (t, *J* = 7.8 Hz, 1H), 7.40 (d, *J* = 7.8 Hz, 2H), 7.33-7.30 (m, 3H), 7.03 (dd, *J* = 3.8 , 1.2 Hz, 1H), 6.92 (dd, *J* = 4.9 , 3.8 Hz, 1H), 2.49 (sept, *J* = 6.8 Hz, 2H), 2.32 (sept, *J* = 6.8 Hz, 2H), 1.38 (d, *J* = 6.9 Hz, 6H), 1.17 (d, *J* = 6.9 Hz, 6H), 1.14 (d, *J* = 6.9 Hz, 6H), 1.07 (d, *J* = 6.7 Hz, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 165.4, 145.9, 145.0, 144.9, 135.5, 132.7, 131.5, 130.9, 128.5, 128.2, 127.9, 125.1, 124.4, 29.2, 29.0, 25.0, 24.6, 24.5, 22.8. HRMS (ESI): calcd for $C_{30}H_{37}CuClN_3S$ ([M+Na]$^+$): *m/z* 592.1585; Found: *m/z* 592.1573.

Complex **9**



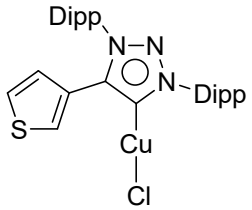
9 was obtained as the black powder (0.29 mmol, 96%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.76 (t, *J* = 7.68 Hz, 1H), 7.73 (t, *J* = 7.92 Hz, 1H), 7.60 (t, *J* = 7.8 Hz , 1H), 7.57 (t, *J* = 7.84 Hz , 1H), 7.46 (d, *J* = 7.84 Hz, 2H), 7.36-7.29 (m, 4H), 7.21 (s, 1H), 2.52 (sept, *J* = 6.8 Hz, 2H), 2.33 (sept, *J* = 6.8 Hz, 2H), 1.16 (d, *J* = 6.8 Hz, 6H), 1.14 (d, *J* = 6.8 Hz, 6H), 1.06 (d, *J* = 6.8 Hz, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 166.9, 145.9, 144.9, 144.0, 139.1, 135.4, 132.9, 131.6, 130.9, 128.4, 126.2, 125.1, 124.7, 124.5, 122.4, 29.3, 29.1, 25.0, 24.6, 24.5,23.0. HRMS (ESI) calcd for $C_{34}H_{39}CuClN_3S$ ([M+Na] $^+$): *m/z* 642.1741; Found: *m/z* 642.1737.

Complex **10**



10 was obtained as the black powder (0.29 mmol, 95%).**^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.01 (d, *J* = 5.6 Hz, 1H), 7.67 (t, *J* = 7.8 Hz, 1H), 7.55 (t, *J* = 7.8 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 7.6 Hz, 2H), 7.27 (t, *J* = 4.8 Hz, 1H), 7.15 (t, *J* = 5.2 Hz, 1H), 2.49 (sept, *J* = 6.8 Hz, 2H), 2.33 (sept, *J* = 6.8 Hz, 2H), 1.38 (d, *J* = 6.8 Hz, 2H), 1.18 (d, *J* = 6.8 Hz, 2H), 1.15 (d, *J* = 6.8 Hz, 2H), 1.11 (d, *J* = 6.8 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): 165.6, 148.9, 146.0, 145.0, 135.4, 134.7, 133.0, 132.7, 131.6, 130.8, 130.6, 130.4, 125.3, 124.4, 29.2, 29.0, 25.1, 24.6, 24.5, 22.9. HRMS (ESI): calcd for:$C_{30}H_{37}ClCuN_3Se$ ([M+Na] $^+$): *m/z* 640.1029; Found: *m/z* 640.1020.

Complex **11**

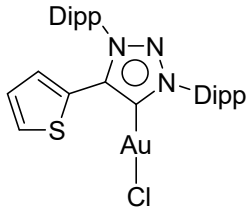


11 was obtained as the white powder (0.29 mmol, 98%).**^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.64, (t, *J* = 7.8 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 1H) 7.40 (d, *J* = 7.8 Hz, 2H), 7.33 (t, *J* = 7.8 Hz, 3H), 7.28 (dd, *J* = 3.0 , 4.8 Hz , 1H), 2.47 (sept, *J* = 6.8 Hz, 2H), 2.31 (sept, *J* = 6.8 Hz, 2H), 1.37 (d, *J* = 6.8 Hz, 6H), 1.17 (d, *J* = 6.8 Hz, 6H), 1.14 (d, *J* = 6.8 Hz, 6H), 1.02 (d, *J* = 6.8 Hz, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 165.5, 145.9, 145.5, 144.9, 135.6, 132.5, 131.5, 131.4, 127.4, 127.2, 126.9, 125.9, 125.1, 124.3, 29.1, 29.0, 24.9, 24.5, 22.8. HRMS (ESI): calcd for $C_{30}H_{37}CuClN_3S$ ([M+Na]$^+$): *m/z* 592.1573; Found: *m/z* 592.1585.

General Procedure for the Preparation of **2-5**

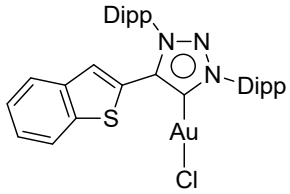
8, **9**, **10** or **11** (0.2 mmol, 1 equiv) was added into the solution of Au(THT)Cl (70.2 mg, 0.22 mmol, 1.1 equiv) in anhydrous CH_2Cl_2 (5.0 mL) in 25mL Schlenk tube at room temperature under argon atmosphere. After that, the mixture was stirred for 3 hours. The resulting mixture was filtered and the filtrate was collected. The volatiles were evaporated under reduced pressure to afford the products. X-ray-quality crystals were obtained by slow diffusion of ether into dichloromethane solution.

Complex **2**



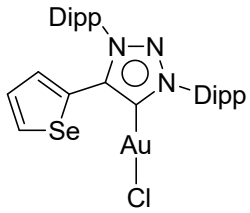
2 was obtained as the white powder (0.2 mmol, 138.6 mg, 99%)..**^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.66 (t, *J* = 7.8 Hz, 1H), 7.55 (t, *J* = 7.8 Hz, 1H), 7.40 (d, *J* = 7.8 Hz, 2H), 7.37 (dd, *J* = 3.6 , 2.8 Hz , 1H), 7.33-7.31 (m, 3H), 6.92 (dd, *J* = 4.0 , 5.2 Hz , 1H), 2.48 (sept, *J* = 6.8 Hz, 2H), 2.33 (sept, *J* = 6.8 Hz, 2H), 1.41 (d, *J* = 8.0 Hz, 6H), 1.15 (t, *J* = 8.0 Hz, 12H), 1.05 (d, *J* = 4.0 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): 160.7, 146.0, 145.1, 143.3, 135.0, 132.9, 131.7, 130.9, 129.4, 129.0, 127.7, 127.0, 125.2, 124.5, 29.3, 29.1, 25.1, 24.5, 24.4, 22.8. HRMS (ESI) calcd for $C_{30}H_{37}AuClN_3S$ ([M+Na]$^+$): *m/z* 726.1954; Found: *m/z* 726.1941.

Complex **3**



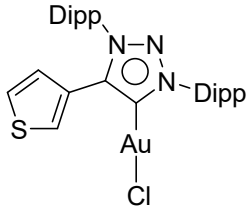
3 was obtained as the white powder (140.2 mg,0.19 mmol, 93%). X-ray-quality crystals were obtained by slow diffusion of ether into dichloromethane solution. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.75-7.71 (m, 2H), 7.67-7.65 (m, 2H), 7.58 (t, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.36 -7.29 (m, 4H), 2.50 (sept, *J* = 6.8 Hz, 2H), 2.37 (sept, *J* = 6.8 Hz, 2H), 1.43 (d, *J* = 6.8 Hz, 6H), 1.17 (t, *J* = 6.8 Hz, 12H), 1.09 (d, *J* = 6.8 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$):161.8, 146.1, 145.1, 143.2, 140.3, 138.7, 135.0, 133.1, 131.8, 130.9, 126.8, 126.4, 126.1, 125.3, 125.1, 124.7, 124.5, 122.3, 29.3, 29.2, 25.1, 24.5, 24.4, 22.9. HRMS (ESI) calcd for $C_{34}H_{39}AuClN_3S$, ([M+Na] $^+$): *m/z* 776.2111; Found: *m/z* 776.2100.

Complex **4**

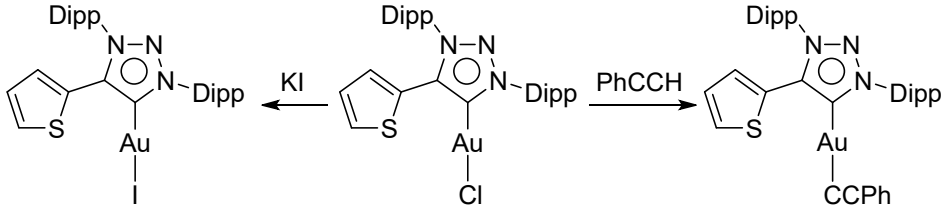


4 was obtained as the white powder (88.6 mg,0.12 mmol, 59%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.01 (d, *J* = 4.0 Hz, 1H), 7.68 (t, *J* = 7.8 Hz, 1H), 7.56 (t, *J* = 7.8 Hz, 1H), 7.42 (d, *J* = 7.8 Hz, 2H), 7.35 - 7.31 (m, 3H), 7.12 (dd, *J* = 5.6 , 4.0 Hz , 1H), 2.48 (sept, *J* = 6.8 Hz , 2H), 2.35 (sept, *J* = 6.8 Hz , 2H), 1.41 (d, *J* = 8.0 Hz, 6H), 1.17 (d, *J* = 4.0 Hz, 6H), 1.15 (d, *J* = 8.0 Hz, 6H), 1.09 (d, *J* = 8.0 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): 161.0, 146.0, 145.1, 135.2, 134.9, 132.9, 131.8, 131.2, 130.9, 130.2, 125.3, 124.5, 29.8, 29.3, 29.1, 25.1, 24.5, 24.4, 22.9. HRMS (ESI) calcd for $C_{30}H_{37}AuClN_3Se$ ([M+Na] $^{+}$): m/z 774.1399; Found: *m/z* 774.1383.

Complex **5**

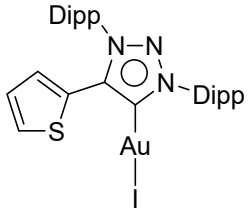


5 was obtained as the white powder (82.6 mg,0.12 mmol, 59%).**^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.71 (q, *J* =1.6 Hz, 1H), 7.65 (t, *J* =7.8 Hz, 1H), 7.57 (t, *J* = 8.0 Hz, 1H), 7.45 (dd, *J* = 5.2 , 1.2 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.25 (m *J* = 4.0 Hz, 1H), 2.47 (sept, *J* = 6.8 Hz , 2H), 2.33 (sept, *J* = 6.8 Hz , 2H), 1.41 (d, *J* = 8.0 Hz, 6H), 1.16 (d, *J* =8.0 Hz, 6H), 1.15 (d, *J* =4.0 Hz, 6H), 1.02 (d, *J* = 8.0 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): 161.0, 145.6, 145.1, 144.0, 135.2, 132.7, 131.7, 131.4, 127.1, 127.0, 126.7, 126.3, 125.2, 124.5, 29.24, 29.18, 25.1, 24.5, 24.4, 22.8. HRMS (ESI) calcd for $C_{30}H_{37}AuClN_3S$ ([M+Na]$^{+}$): *m/z* 726.1954; Found: *m/z* 726.1948.



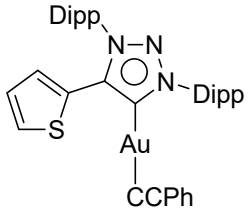
6 **2** **7**

Complex **6**



Under argon atmosphere, KI (33.2 mg, 0.2 mmol, 1 equiv) was added into the solution of **2** (140.0 mg, 0.2 mmol, 1 equiv) in CH_2Cl_2 (5.0 mL) in a Schlenk tube at room temperature. After 30 mins, the contents were filtered and volatiles were evaporated under reduced pressure. The solid was washed twice with methylbenzene twice to give final product complex **6** as white powder (164.4 mg, 0.18 mmol, 88%).**^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.68 (t, *J* = 7.8 Hz, 1H), 7.57 (t, *J* = 7.8 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.38 (dd, *J* = 2.8, 0.8 Hz , 1H), 7.34-7.32 (m, 3H), 6.93-6.90 (m, 1H), 2.51 (sept, *J* = 6.8 Hz , 2H), 2.33 (sept, *J* = 6.8 Hz , 2H), 1.41 (d, *J* = 8.0 Hz, 6H), 1.17 (d, *J* = 4.0 Hz, 6H), 1.15 (d, *J* = 8.0 Hz, 6H), 1.07 (d, *J* = 4.0 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): 171.1, 146.0, 145.1, 143.0, 135.0, 132.9, 131.7, 130.9, 129.2, 128.9, 127.7, 127.3, 125.2,124.4, 29.3, 29.1, 25.1, 24.6, 24.4, 22.8. HRMS (ESI) calcd for $C_{30}H_{37}AuIN_3S$ ([M+Na]$^+$): *m/z* 818.1311; Found: *m/z* 818.1302.

Complex **7**



Under argon atmosphere, phenylacetylene (56.0μL, 0.5 mmol, 2.5 equiv) was added into the solution of **2** (140.0 mg, 0.2 mmol, 1 equiv) and KOBu^t (89.6 mg, 0.8 mmol, 4 equiv) in CH_3OH (30.0 mL) and the mixture was stirred at room temperature for 12 h. Then the mixture was filtered and volatiles were evaporated under reduced pressure. The residue was washed with diethyl ether (4x2 ml) to give the product as white powder **7** (146.3 mg, 0.19 mmol, 95%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.65 (t, *J* = 7.8 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 1H), 7.45 (d, *J* = 4.0 Hz, 1H) , 7.43 (d, *J* = 8.0 Hz, 2H) ,7.39 (d, *J* = 7.8 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 2H), 7.29(d, *J* = 8.0 Hz, 1H), 7.18 (d, *J* = 4.0 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 7.10 (t, *J* = 8.0 Hz, 1H), 6.91 (t, *J* = 4.0 Hz, 1H), 2.51 (sept, *J* = 6.8 Hz , 2H), 2.32 (sept, *J* = 6.8 Hz, 2H), 1.43 (d, *J* = 6.8 Hz, 6H),1.16 (d, *J* =6.8 Hz, 6H), 1.14 (d, *J* =6.8 Hz, 6H), 1.05 (d, *J* = 6.8 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$):176.6, 145.9, 145.0, 144.7, 135.1, 132.6, 132.3, 131.4, 130.8, 129.4, 128.7, 127.6, 127.5, 126.2, 125.8, 125.0, 124.2, 104.6, 29.1, 29.0, 25.0, 24.4, 22.7. HRMS (ESI) calcd for $C_{38}H_{42}AuN_3S$ ([M+H] $^+$): *m/z* 770.2838; Found: *m/z* 770.2831.

2. **Morphology characterization**

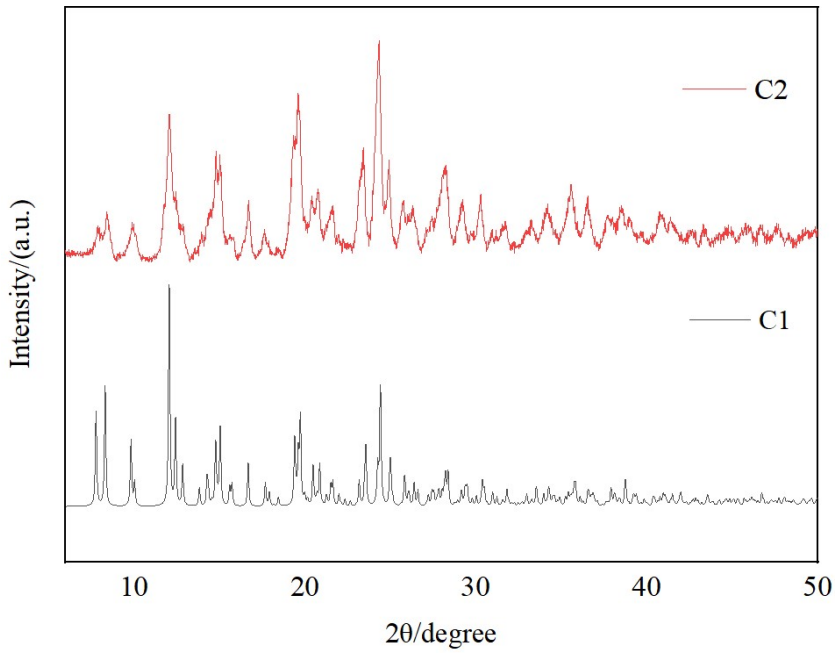


Figure S1. Powder XRD pattern of the complex **2** (red curve) and the PXRD pattern of complex **2** (black curve) by fitted value.

3. **Crystallographic details**

For complex **2** (CCDC 2405235), during the structure refinement process, disorder was observed for the Au-Cl part and the five-membered ring, which seem to switch between two positions. However, only one part of the ring could be modeled with two disordered orientations on one side, with an occupancy of approximately 95%. Although several Q peaks are present around the Au1-Cl (Figure S2), they do not form a reasonable geometric arrangement. The remaining 5% portion is challenging to model on the other side, likely also exhibiting two disordered orientations. The final refined structure appears to be a mixture of two molecular species; however, it is more likely that only one species exists in the crystal structure. The difficulty in modeling the ring with extremely low occupancy contributes to this apparent complexity.

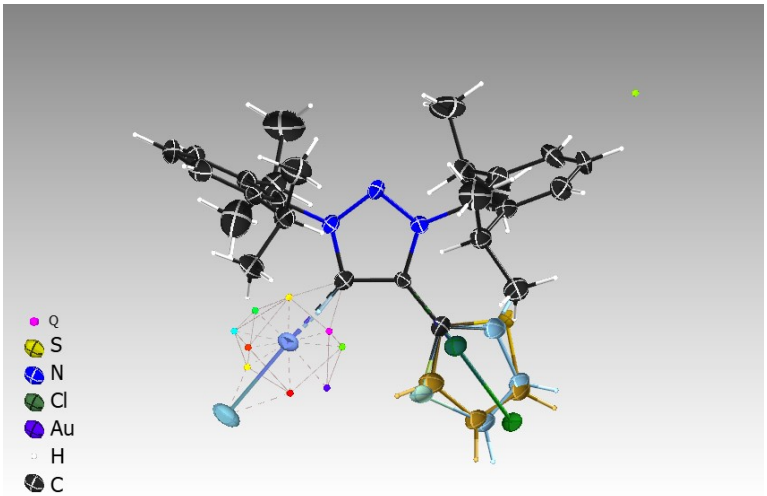


Figure S2. the structure refinement process of **2**.

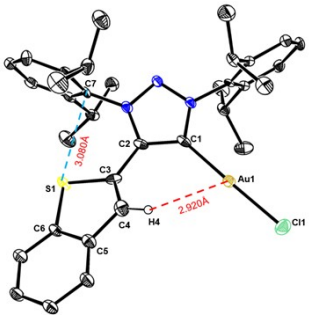


Figure S3. ORTEP diagram of crystal structure of **3** in the other orientation with an occupancy ratio 42:58. (Ellipsoids are drawn at the 50% probability level; Hydrogen atoms except H4 in the other orientation have been omitted for clarity).

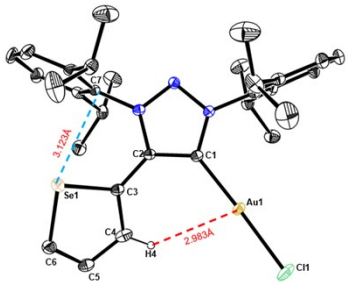


Figure S4. ORTEP diagram of crystal structure of **4** in the other orientation with an occupancy ratio 83:11. (Ellipsoids are drawn at the 50% probability level; Hydrogen atoms except H4 in the other orientation have been omitted for clarity).

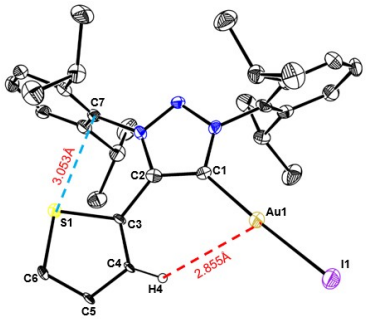


Figure S5. ORTEP diagram of crystal structure of **6** in the other orientation with an occupancy ratio 62:25. (Ellipsoids are drawn at the 50% probability level; Hydrogen atoms except H4 in the other orientation have been omitted for clarity).

During the structure refinement of complex **6** (CCDC 2405250), a problem similar to that of complex **2** was encountered. While a disordered ring was suspected to be present on the opposite side, it was difficult to model based on the Q peaks surrounding the Au1-I1 which was exhibited as the following Figure S6. The "unmodeled" portion, which has an occupancy of approximately 13%, likely exhibits two disordered orientations, akin to those observed on the other side. However, the weak signal made it impossible to establish a reasonable disorder model. The final

refined structure seemingly represents a mixture of two molecular species; nevertheless, it is more likely that only a single species exists in the crystal structure.

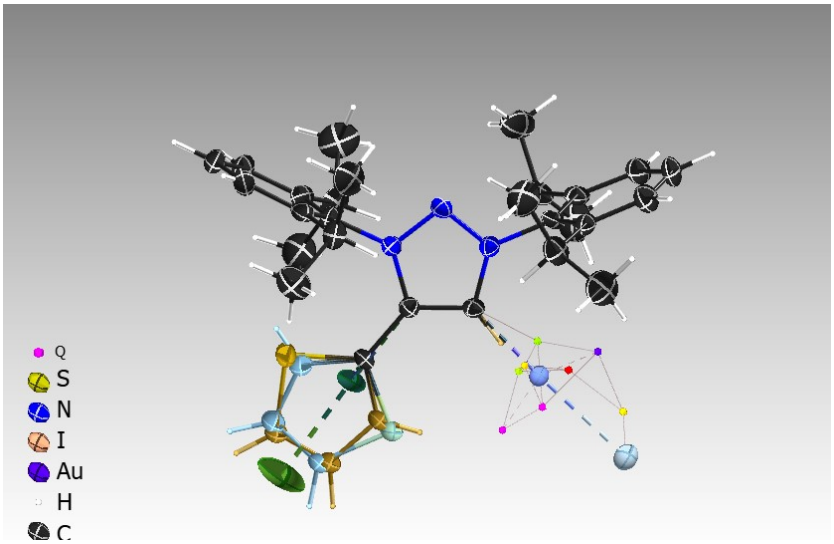


Figure S6. the structure refinement process of **6**.

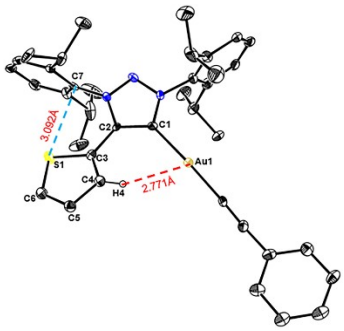


Figure S7. ORTEP diagram of crystal structure of **7** in the other orientation with two different orientations in 43:57 ratio. (Ellipsoids are drawn at the 50% probability level; Hydrogen atoms except H4 in the other orientation have been omitted for clarity).

Table S1. Selected Bond Lengths [Å], Angles, and Dihedral Angles [°] of **2**, **3**, **5**, **6**, **7** in the other orientation.

bonds [Å],angles [°]	**2**	**3**	**5**	**6**	**7**
H4···Au1	2.918	2.920	2.865	2.855	2.769
S1···C7	3.086	3.080	4.621	3.055	3.092
C6-S1···C7	147.71	151.7(6)	-	165.0(8)	160(1)
C4-H4···Au1	116.39	126.73	122.92	132.15	132.98
C4-C3-C2-C1	24.(5)	24.(1)	-30.1(3)	-11.1(12)	16(2)
S2-C3-C2-C1	148.93	-157.5(4)	-	167.1(7)	-165.7(7)

S1-C6-C3-C2	-	-	-174.4(2)	-	-

Compound **1**

Table S2. Crystal data and structure refinement for **1**

CCDC Number	2405319
Empirical formula	$C_{63}H_{80}AuCl_7N_6S_2$
Formula weight	1430.56
Temperature [K]	116(2)
Crystal system	monoclinic
Space group (number)	$P2_1/n$ (14)
a [Å]	13.8322(3)
b [Å]	23.6472(6)
c [Å]	21.1792(5)
α [°]	90
β [°]	91.678(2)
γ [°]	90
Volume [Å^3]	6924.6(3)
Z	4
ρ_{calc} [gcm^{-3}]	1.372
μ [mm^{-1}]	2.496
F(000)	2920
Crystal size [mm^3]	0.350×0.350×0.090
Crystal colour	clourless
Crystal shape	block
Radiation	MoK_α (λ=0.71073 Å)
2θ range [°]	6.14 to 52.00 (0.81 Å)
Index ranges	−17 ≤ h ≤ 16 −25 ≤ k ≤ 29 −23 ≤ l ≤ 25
Reflections collected	42785
Independent reflections	13345

	R_{int} = 0.0756 R_{sigma} = 0.0899
Completeness to θ = 25.242°	99.7 %
Data / Restraints / Parameters	13345/63/756
Goodness-of-fit on F^2	1.042
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0534 wR_2 = 0.1081
Final *R* indexes [all data]	R_1 = 0.0832 wR_2 = 0.1236
Largest peak/hole [eÅ^{-3}]	1.49/-1.14

Complex **2**

Table S3 Crystallographic data and refinement parameters for complex **2**

CCDC Number	2405235
Empirical formula	$C_{29.79}H_{36.90}AuClN_3S_{0.95}$
Formula weight	699.95
Temperature [K]	150(2)
Crystal system	triclinic
Space group (number)	$P\bar{1}$ (2)
a [Å]	10.1390(10)
b [Å]	13.1189(13)
c [Å]	13.2117(13)
α [°]	107.881(3)
β [°]	102.790(3)
γ [°]	108.608(3)
Volume [Å^3]	1482.3(3)
Z	2
ρ_{calc} [gcm^{-3}]	1.568
μ [mm^{-1}]	5.142
F(000)	696
Crystal size [mm^3]	0.160×0.150×0.120
Crystal colour	colourless
Crystal shape	block
Radiation	MoK_α (λ=0.71073 Å)

2θ range [°]	4.46 to 50.70 (0.83 Å)
Index ranges	−12 ≤ h ≤ 12 −15 ≤ k ≤ 15 −15 ≤ l ≤ 15
Reflections collected	22682
Independent reflections	5365 R_{int} = 0.1079 R_{sigma} = 0.1007

Complex **3**

Table S4 Crystallographic data and refinement parameters for complex **3**

CCDC Number	2405236
Empirical formula	$C_{34}H_{39}AuClN_3S$
Formula weight	754.16
Temperature [K]	117(2)
Crystal system	triclinic
Space group (number)	$P\bar{1}$ (2)
a [Å]	10.5521(4)
b [Å]	11.9537(5)
c [Å]	14.4742(6)
α [°]	93.583(3)
β [°]	107.583(4)
γ [°]	111.135(4)
Volume [Å^3]	1592.90(12)
Z	2
ρ_{calc} [gcm^{-3}]	1.572
μ [mm^{-1}]	4.794
F(000)	752
Crystal size [mm^3]	0.380×0.330×0.210
Crystal colour	colourless
Crystal shape	block
Radiation	MoK_α (λ=0.71073 Å)
2θ range [°]	5.85 to 52.00 (0.81 Å)
Index ranges	−13 ≤ h ≤ 12 −14 ≤ k ≤ 14 −17 ≤ l ≤ 17

Reflections collected	20578
Independent reflections	6232 R_{int} = 0.0605 R_{sigma} = 0.0711

Complex **4**

Table S5 Crystallographic data and refinement parameters for complex **4**

CCDC Number	2405244
Empirical formula	$C_{30}H_{37}AuClN_3Se$
Formula weight	751.00
Temperature [K]	150(2)
Crystal system	triclinic
Space group (number)	$P\bar{1}$ (2)
a [Å]	10.2524(7)
b [Å]	13.1157(8)
c [Å]	13.1894(7)
α [°]	106.567(2)
β [°]	104.031(2)
γ [°]	109.117(2)
Volume [Å^3]	1491.66(16)
Z	2
ρ_{calc} [gcm^{-3}]	1.672
μ [mm^{-1}]	6.263
F(000)	736
Crystal size [mm^3]	0.100×0.100×0.050
Crystal colour	colourless
Crystal shape	block
Radiation	MoK_α (λ=0.71073 Å)
2θ range [°]	4.42 to 56.73 (0.75 Å)
Index ranges	−13 ≤ h ≤ 13 −17 ≤ k ≤ 17 −17 ≤ l ≤ 15

Reflections collected	32071
Independent reflections	7445 R_{int} = 0.0890 R_{sigma} = 0.0786

Complex **5**

Table S6 Crystallographic data and refinement parameters for complex **5**

CCDC Number	2405248
Empirical formula	$C_{30}H_{37}AuClN_3S$
Formula weight	704.10
Temperature [K]	150(2)
Crystal system	monoclinic
Space group (number)	$P\bar{1}$ (2)
a [Å]	9.3785(4)
b [Å]	12.1907(5)
c [Å]	14.6726(6)
α [°]	65.5960(10)
β [°]	84.7140(10)
γ [°]	72.1160(10)
Volume [Å^3]	1452.66(11)
Z	2
ρ_{calc} [gcm^{-3}]	1.610
μ [mm^{-1}]	5.251
F(000)	700
Crystal size [mm^3]	0.200×0.200×0.200
Crystal colour	colourless
Crystal shape	block
Radiation	MoK_α (λ=0.71073 Å)
2θ range [°]	4.57 to 61.04 (0.70 Å)
Index ranges	−13 ≤ h ≤ 13 −17 ≤ k ≤ 17 −20 ≤ l ≤ 20
Reflections collected	45146
Independent reflections	8841 R_{int} = 0.0441 R_{sigma} = 0.0341

Completeness to θ = 25.242°	99.5 %
Data / Restraints / Parameters	8841/0/333
Goodness-of-fit on F^2	1.027
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0204 wR_2 = 0.0465
Final *R* indexes [all data]	R_1 = 0.0225 wR_2 = 0.0472
Largest peak/hole [eÅ^{-3}]	0.59/-1.35
Completeness to θ = 25.242°	99.5 %
Data / Restraints / Parameters	8841/0/333
Goodness-of-fit on F^2	1.027
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0204 wR_2 = 0.0465
Final *R* indexes [all data]	R_1 = 0.0225 wR_2 = 0.0472
Largest peak/hole [eÅ^{-3}]	0.59/-1.35

Complex **6**

Table S7 Crystallographic data and refinement parameters for complex **6** (pbca)

CCDC Number	2405250
Empirical formula	$C_{29.87}H_{36.87}AuIN_3S$
Formula weight	793.81
Temperature [K]	150(2)
Crystal system	orthorhombic
Space group (number)	$Pbca$ (61)
a [Å]	18.1203(6)
b [Å]	15.6207(5)
c [Å]	21.3516(5)
α [°]	90
β [°]	90
γ [°]	90
Volume [Å^3]	6043.6(3)
Z	8
ρ_{calc} [gcm^{-3}]	1.745
μ [mm^{-1}]	5.981
F(000)	3081

Crystal size [mm^3]	0.160×0.150×0.120
Crystal colour	colourless
Crystal shape	plate
Radiation	MoK_α (λ=0.71073 Å)
2θ range [°]	3.94 to 54.98 (0.77 Å)
Index ranges	−23 ≤ h ≤ 23 −20 ≤ k ≤ 20 −27 ≤ l ≤ 27
Reflections collected	59289
Independent reflections	6939 R_{int} = 0.0936 R_{sigma} = 0.0472

Complex **7**

Table S8 Crystallographic data and refinement parameters for complex **7**

CCDC Number	2405254
Empirical formula	$C_{38}H_{42}AuN_3S$
Formula weight	769.77
Temperature / K	116.45(10)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a / Å, b / Å, c / Å	11.6884(8), 16.9218(8), 17.0507(7)
α/°, β/°, γ/°	90.00, 90.00, 90.00
Volume / $Å^3$	3372.4(3)
Z	4
ρ_{calc} / mg mm^{-3}	1.516
μ / mm^{-1}	4.454
F(000)	1544
Crystal size / mm^3	0.32 × 0.29 × 0.23
2Θ range for data collection	5.92 to 52°
Index ranges	-14 ≤ h ≤ 14, -15 ≤ k ≤ 20, -21 ≤ l ≤ 14
Reflections collected	15657
Independent reflections	6485[R(int) = 0.0493 (inf-0.9Å)]
Data/restraints/parameters	6485/135/433
Goodness-of-fit on F^2	1.024

Final R indexes [I>2σ (I) i.e. F_o>4σ (F_o)]	R_1 = 0.0402, wR_2 = 0.0650
Final R indexes [all data]	R_1 = 0.0485, wR_2 = 0.0691
Largest diff. peak/hole / e Å^{-3}	1.466/-1.029
Flack Parameters	-0.010(8)
Completeness	0.9965

4. **Photophysical characterizations**

Complex **2**

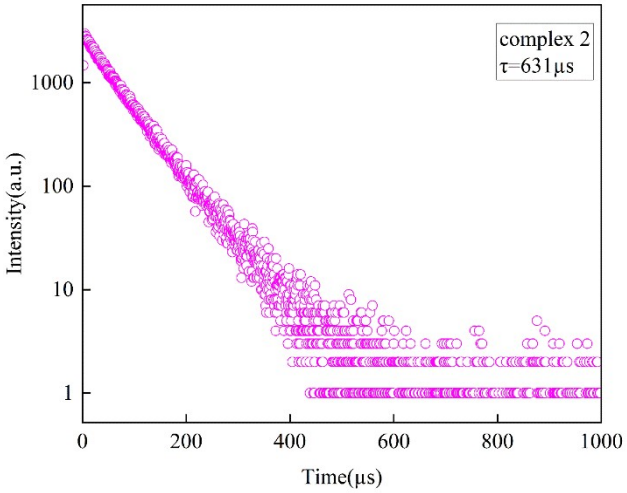
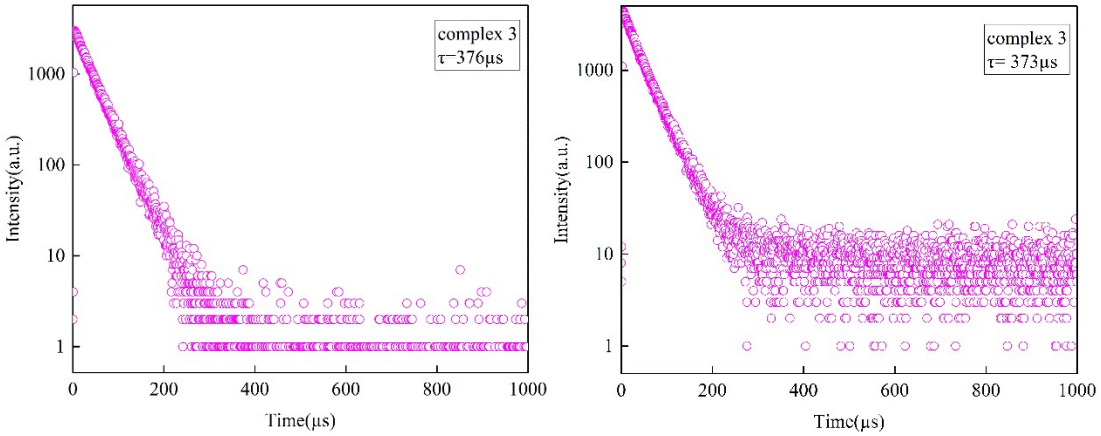


Figure S8. Transient PL decay curves of **2** in 10^{-5} M DCM solution at λ_{em} =520 nm

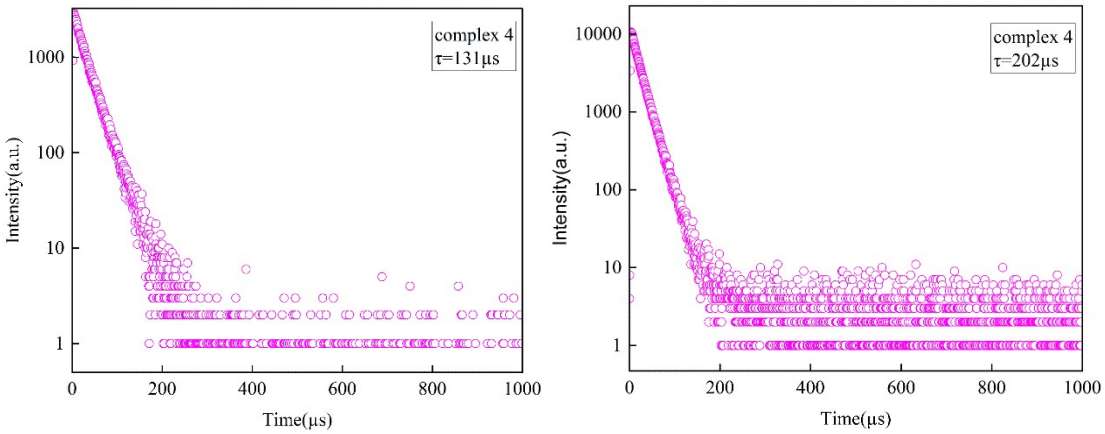
Complex **3**



λ_{em}= 520 nm λ_{em}=620 nm

Figure S9. Transient PL decay curves of **3** in 10^{-5} M DCM solution at λ_{em}=520 nm,λ_{em}=620 nm.

Complex **4**



λ_{em}= 520 nm λ_{em}=620 nm

Figure S10. Transient PL decay curves of **4** in 10^{-5} M DCM solution at λ_{em}=520 nm,λ_{em}=620 nm.

Complex **5**

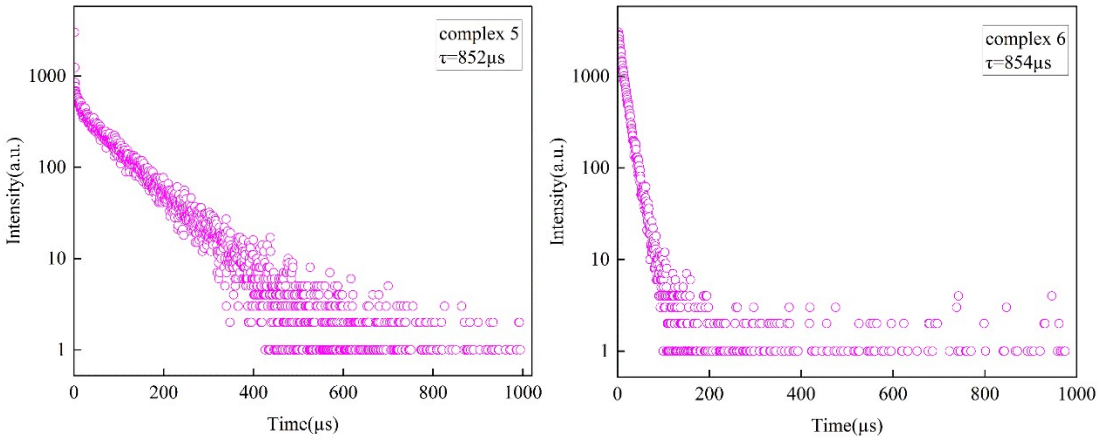


Figure S11. Transient PL decay curves of **5** and **6** in 10^{-5} M DCM solution both at around λ_{em} =520 nm.

Complex **7**

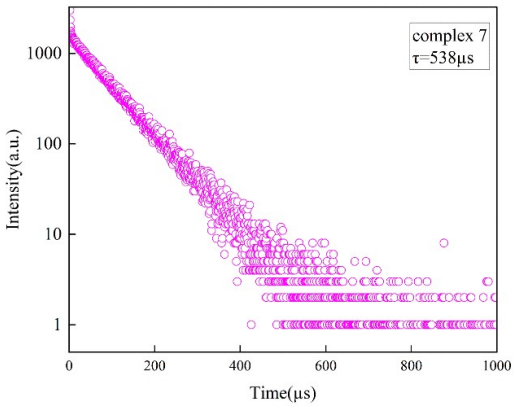


Figure S12. Transient PL decay curves of **7** in 10^{-5} M DCM solution both at λ_{em} =520 nm plotted Origin 2024 diagram.

5. **References**

1. Huang, S.; Wu, Y.; Huang, L.; Hu, C.; Yan, X. Synthesis, Characterization and Photophysical Properties of Mesoionic *N*-Heterocyclic Imines. *Chem Asian J*. **2022**, 17, e202200281

2. Bouffard, J.; Keitz, B. K.; Tonner, R.; Guisado-Barrios, G.; Frenking, G.; Grubbs, R. H.; Bertrand, G. Synthesis of Highly Stable 1,3-Diaryl-1H-1,2,3-triazol-5-ylidenes and Their Applications in Ruthenium-Catalyzed Olefin Metathesis. *Organometallics* **2011**, 30, 2617-2627.

6. **NMR spectra**

Figure S13: ^{1}H-NMR spectrum of **L1-(H^{+})** in $CDCl_3$

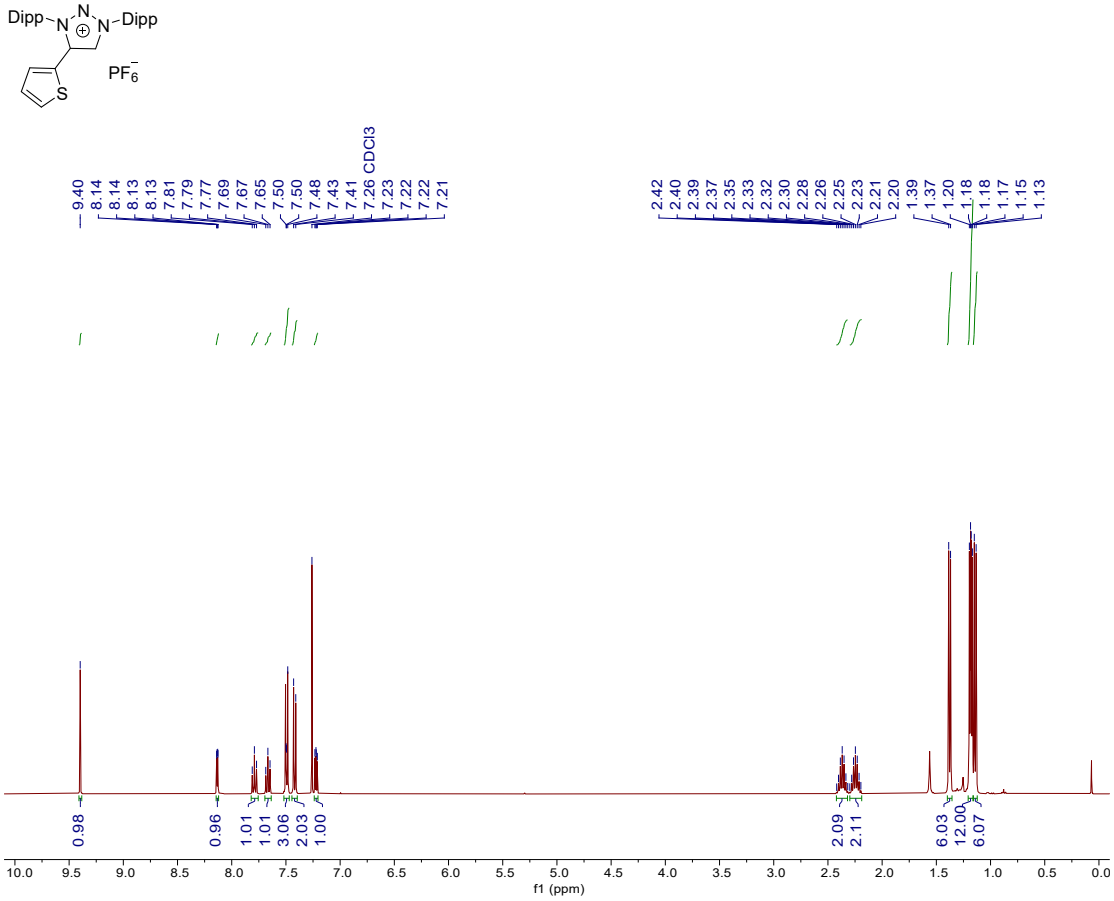
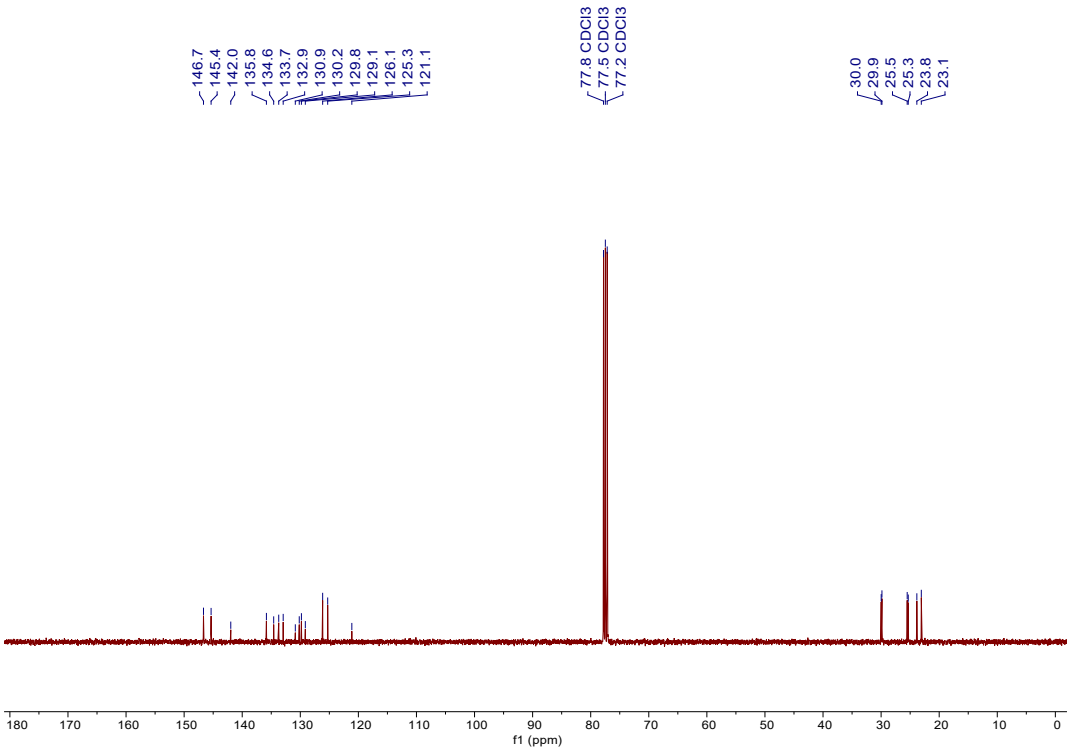


Figure S14: ^{13}C-NMR spectrum of **L1-(H^{+})** in $CDCl_3$



Figures S15: ^{1}H-NMR spectrum of **1** in $CDCl_3$

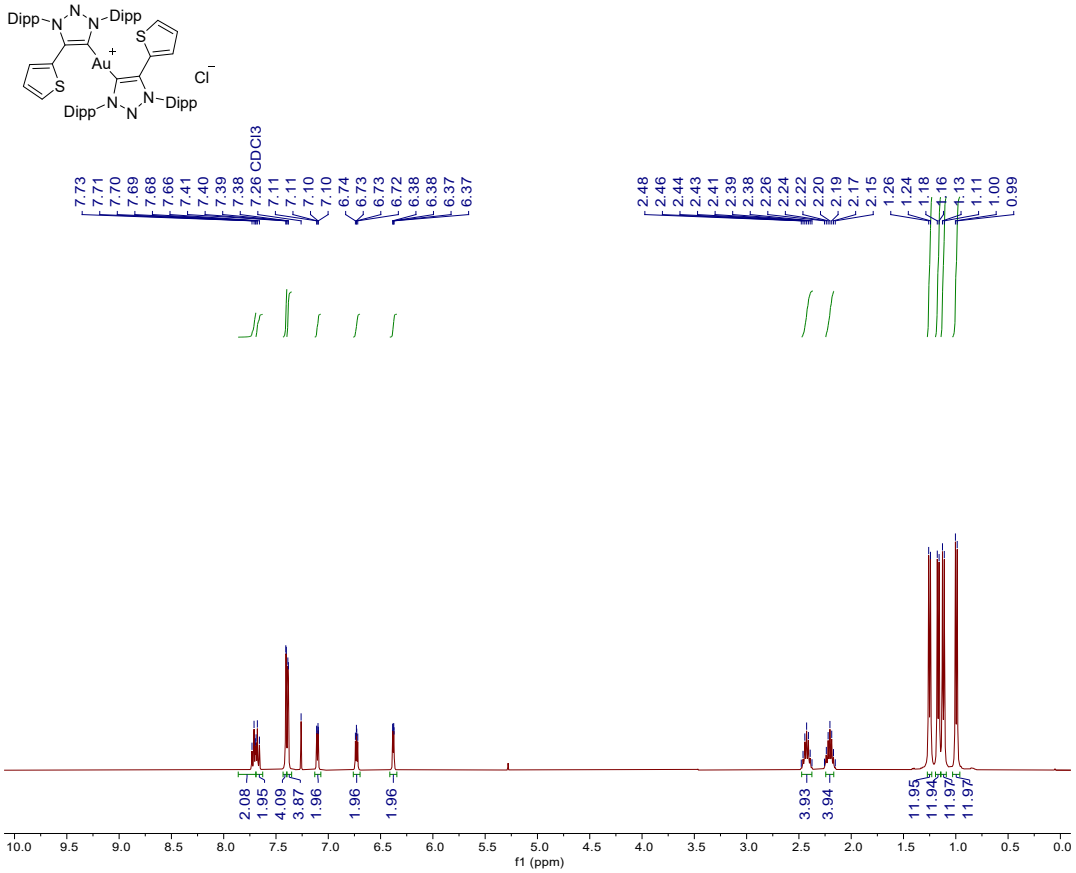
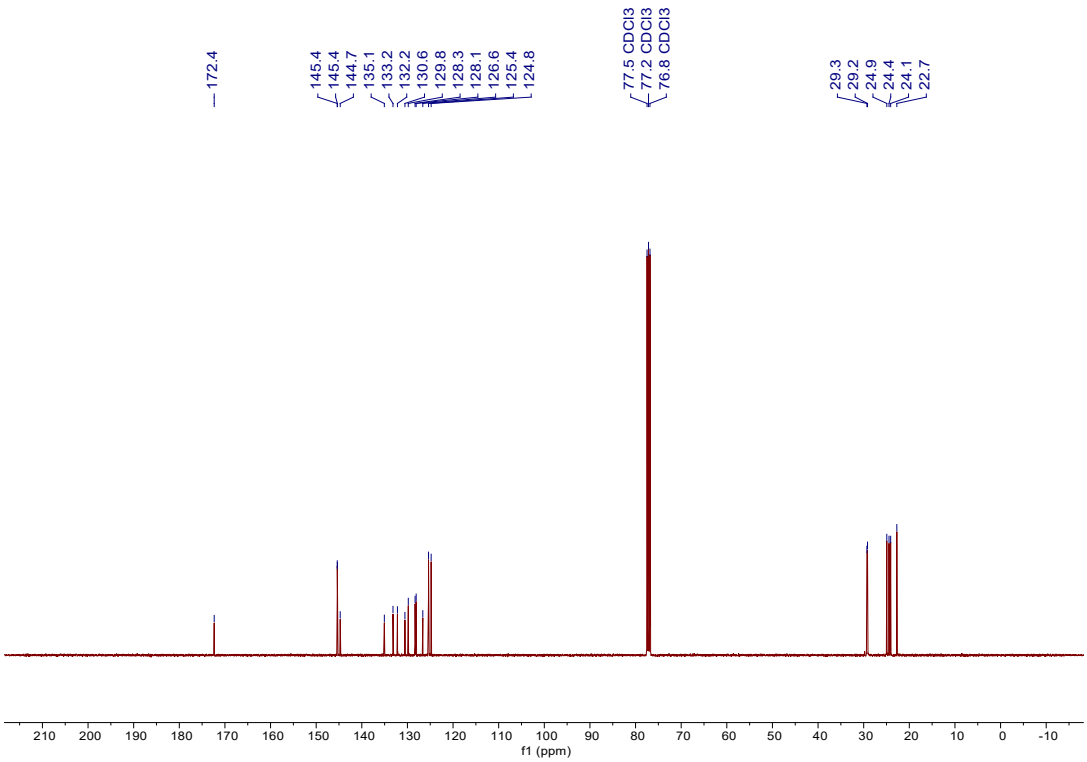
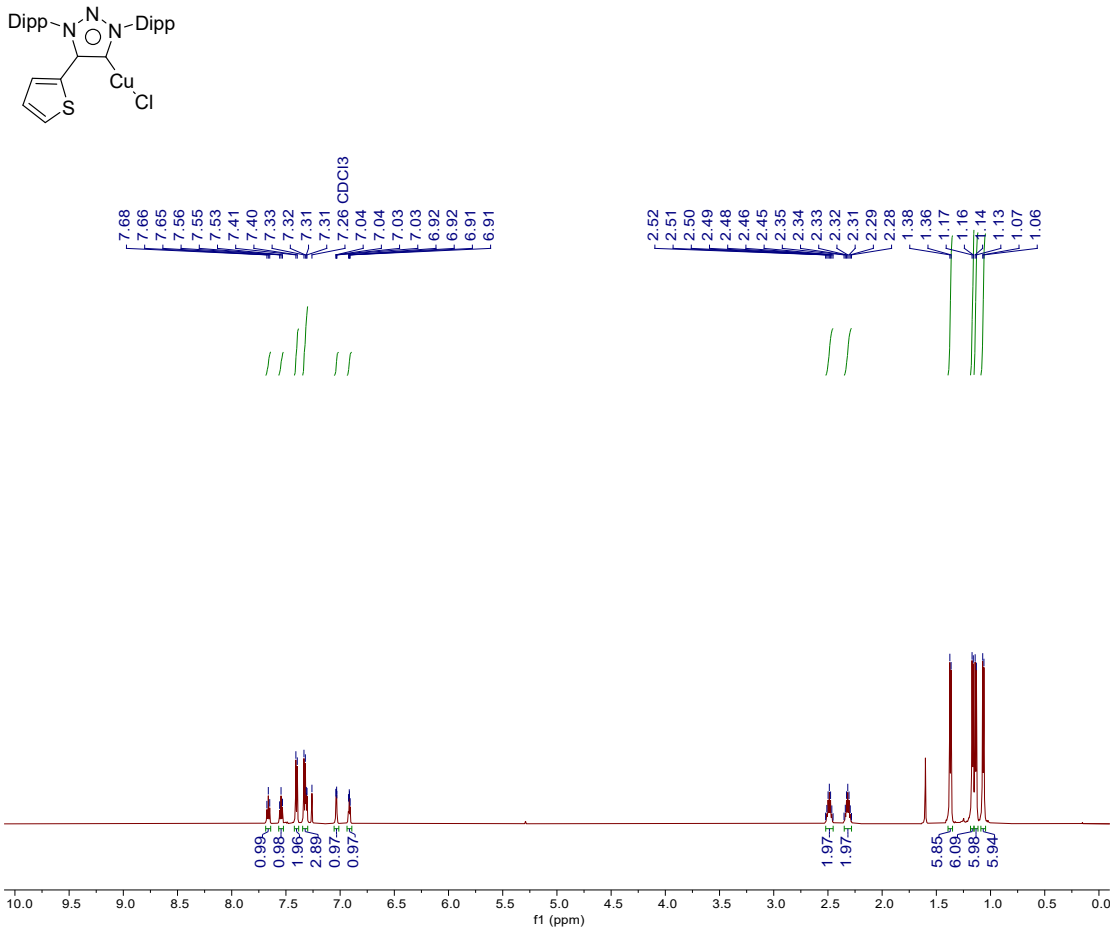


Figure S16:^{13}C-NMR spectrum of **1** in $CDCl_3$



Figures S17: ^{1}H-NMR spectrum of **8** in $CDCl_3$



Figures S18:^{13}C-NMR spectrum of **8** in $CDCl_3$

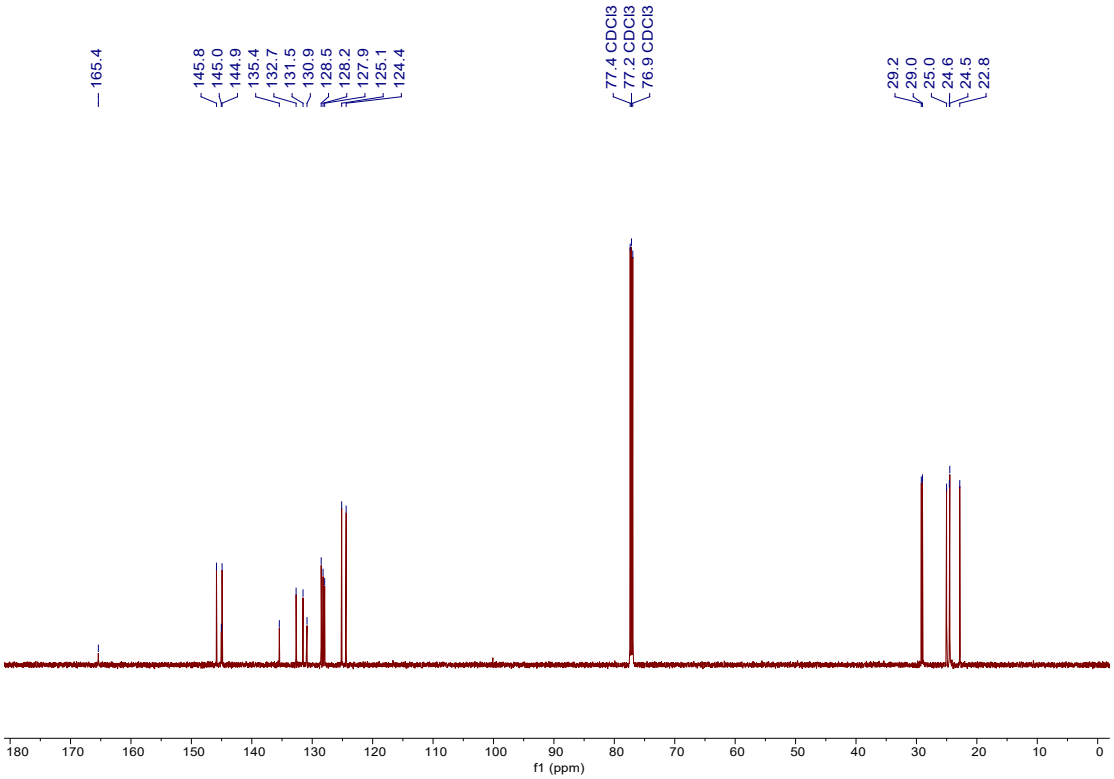
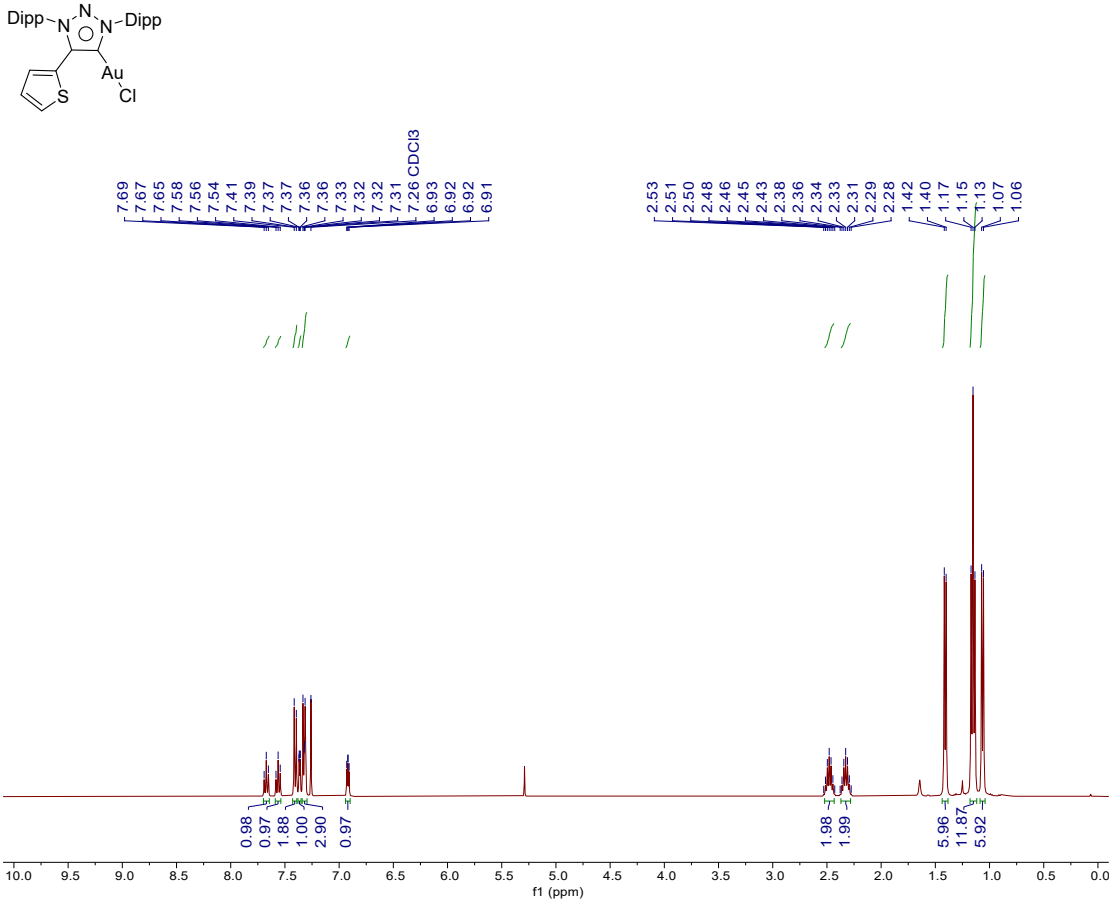


Figure S19:^{1}H-NMR spectrum of **2** in $CDCl_3$



Figures S20: ^{13}C-NMR spectrum of **2** in $CDCl_3$

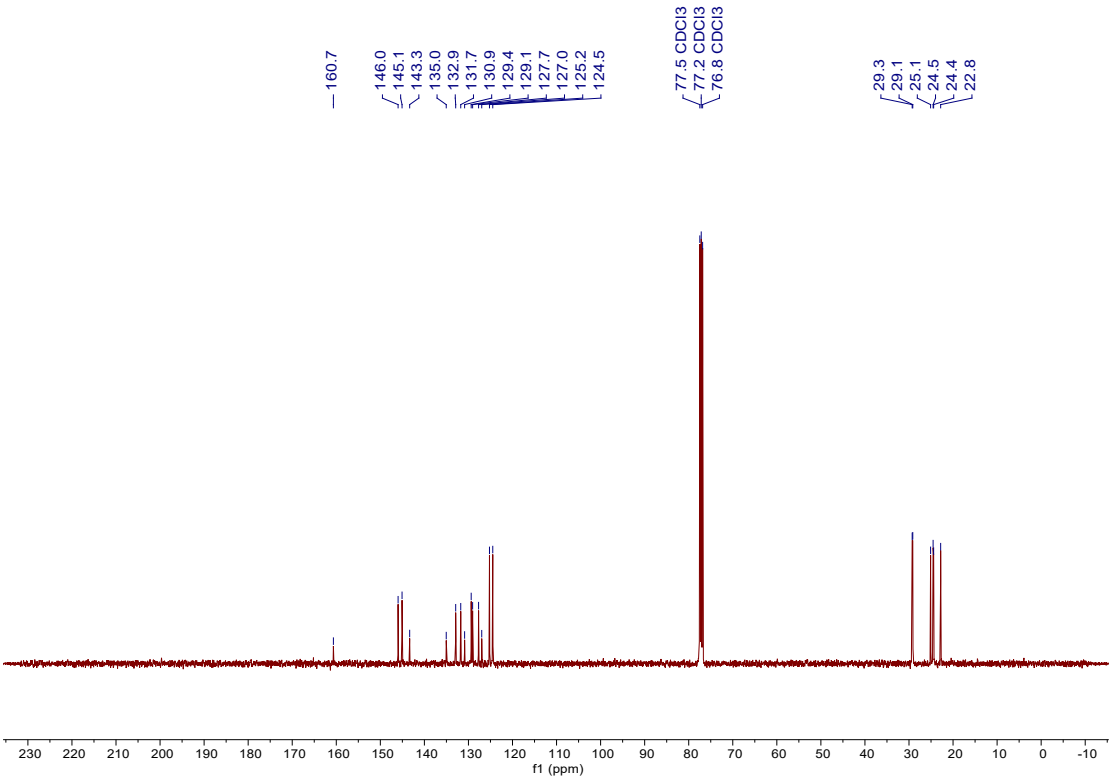


Figure S21: ^{1}**H-NMR** spectrum of **L2-(H^{+})** in $CDCl_3$

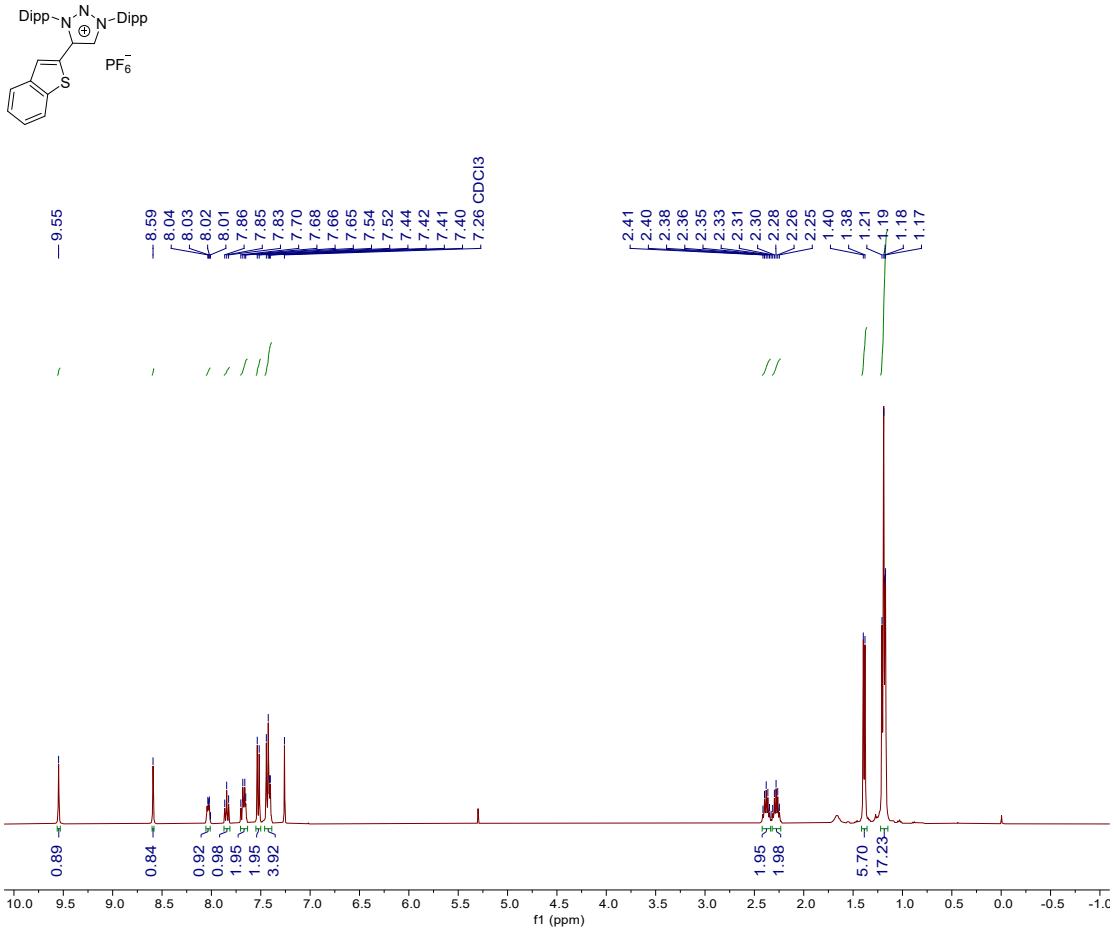


Figure S22: ^{13}**C-NMR** spectrum of **L2-(H^{+})** in $CDCl_3$

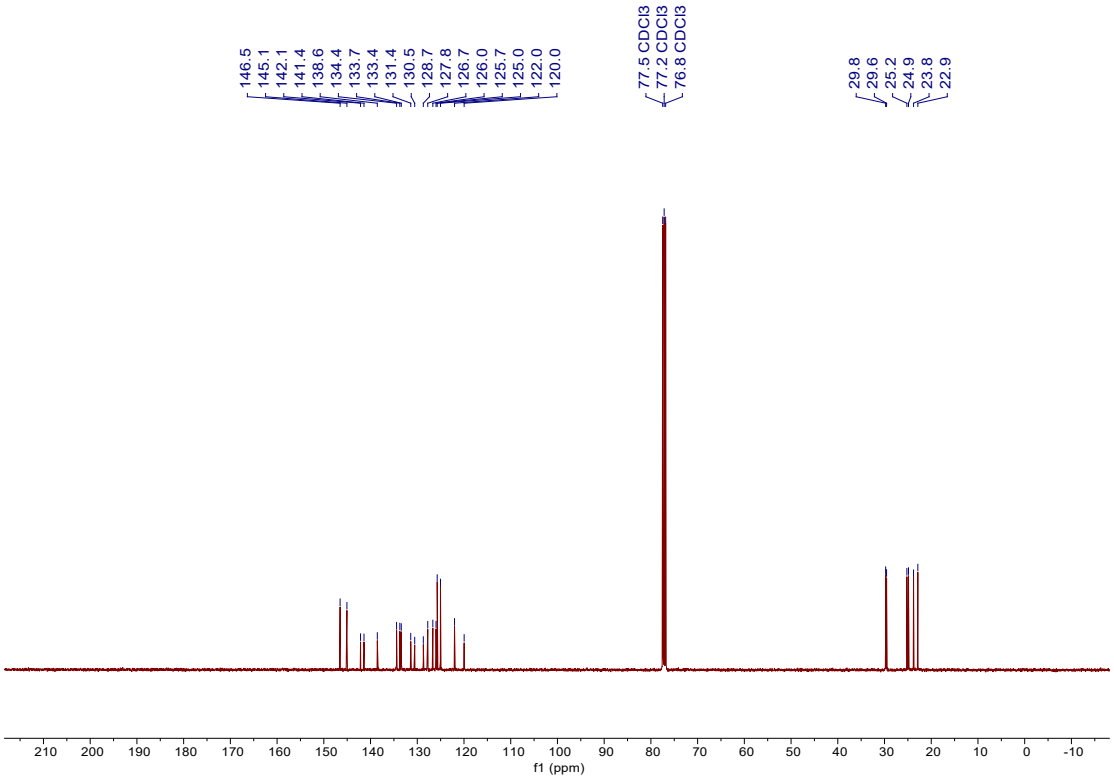


Figure S23:^{1}H-NMR spectrum of **9** in $CDCl_3$

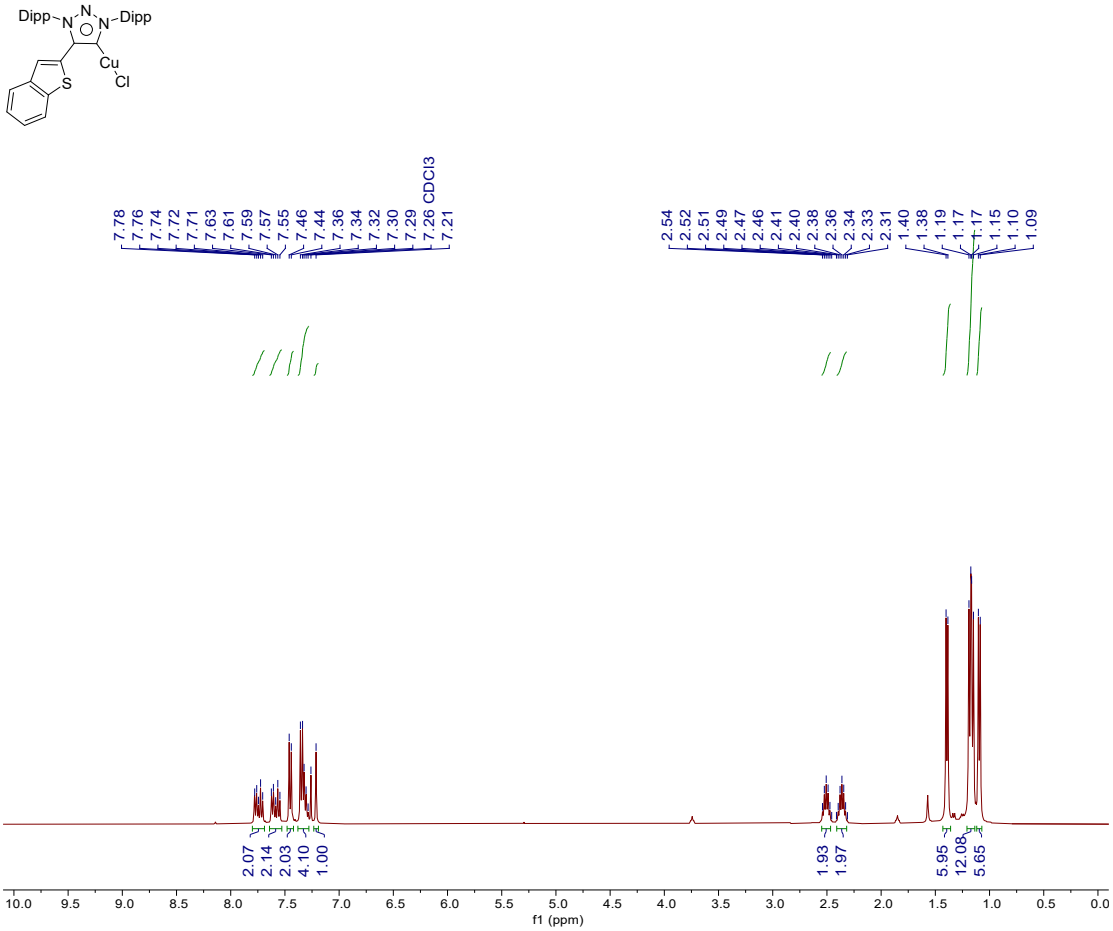


Figure S24:^{13}C-NMR spectrum of **9** in $CDCl_3$

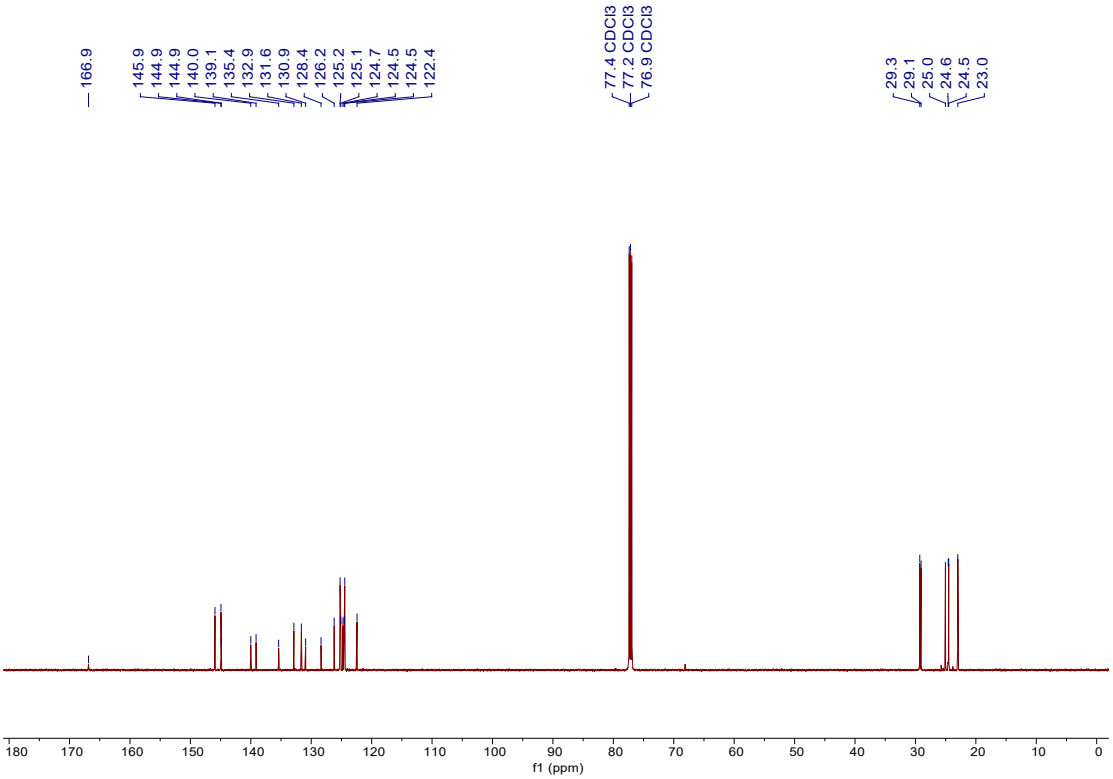


Figure S25:^{1}H-NMR spectrum of **3** in $CDCl_3$

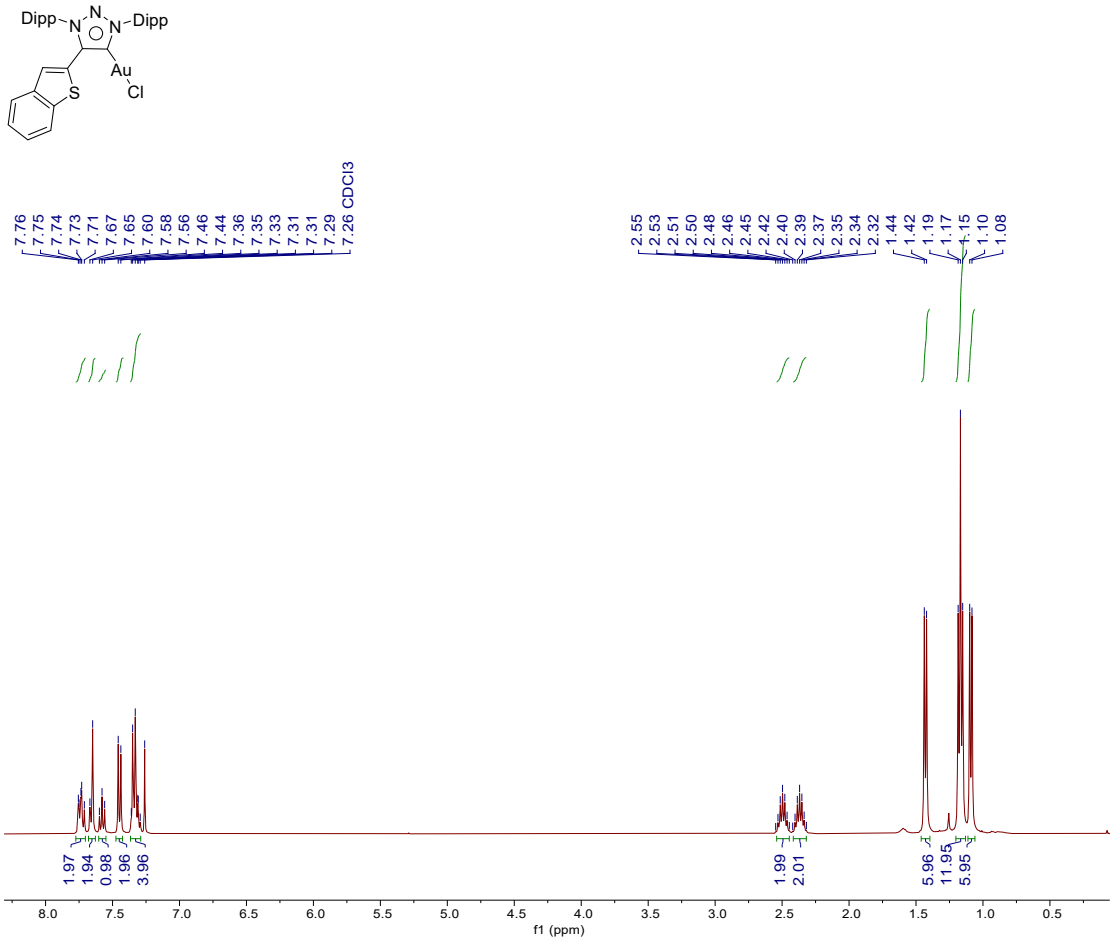


Figure S26:^{13}C-NMR spectrum of **3** in $CDCl_3$

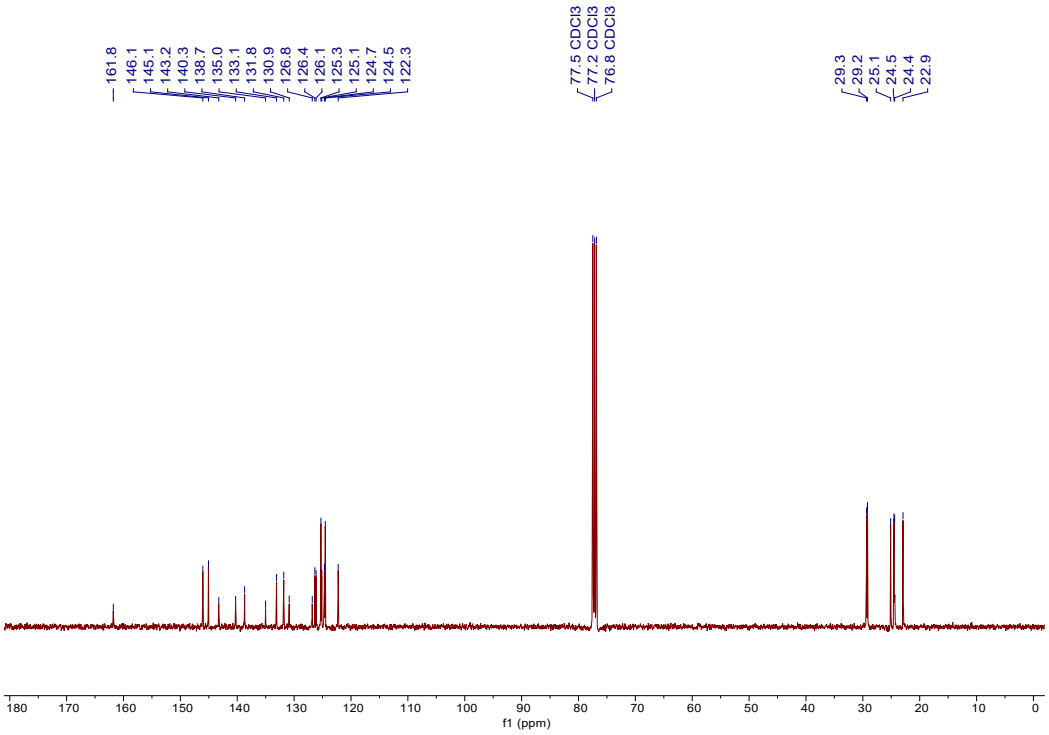


Figure S27:^{1}H-NMR spectrum of **L3-(H^{+})** in $CDCl_3$

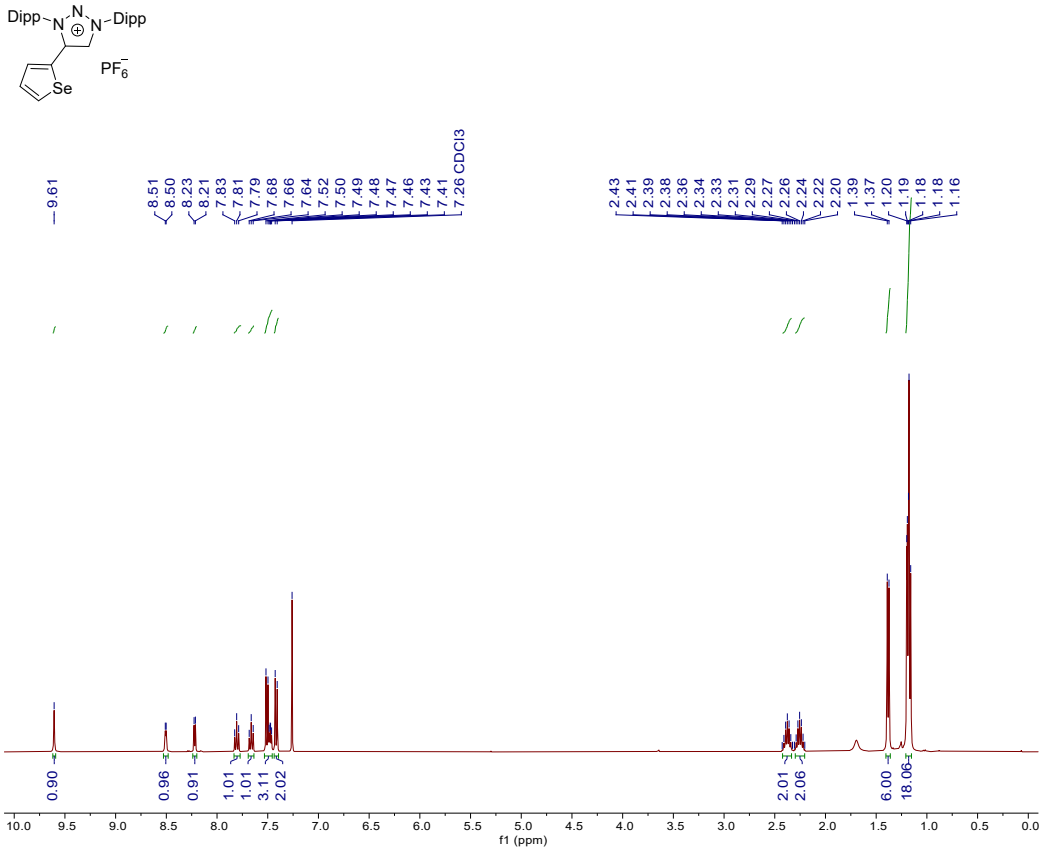


Figure S28:^{13}C-NMR spectrum of **L3-(H^{+})** in $CDCl_3$

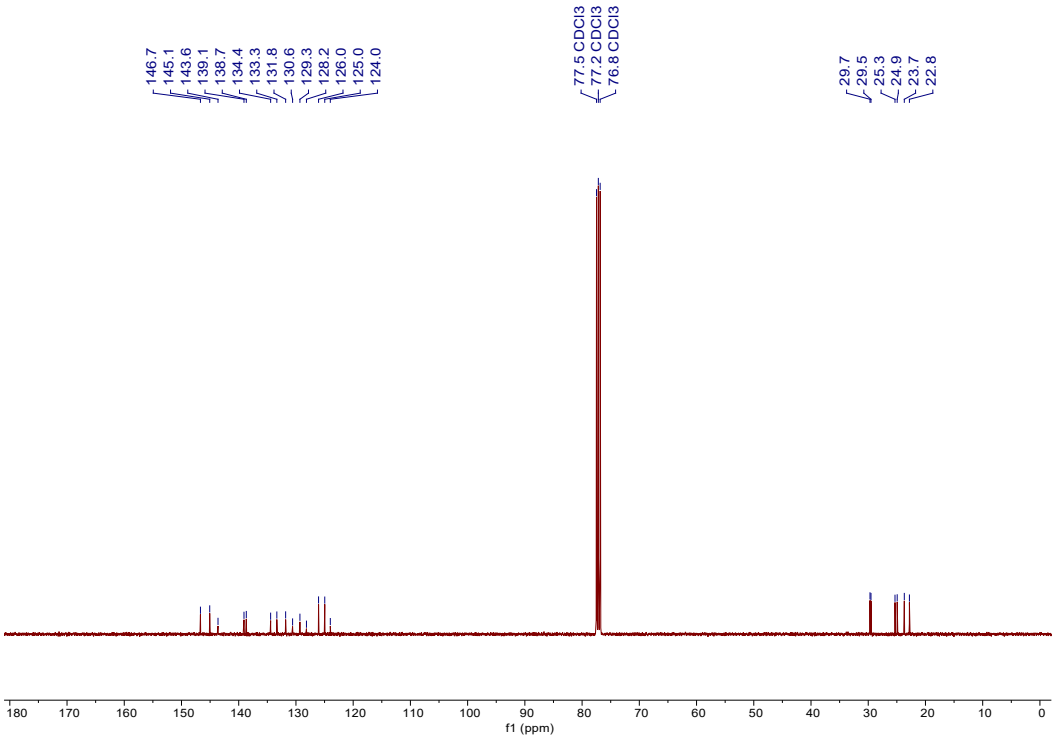


Figure S29:^{1}H-NMR spectrum of **10** in $CDCl_3$

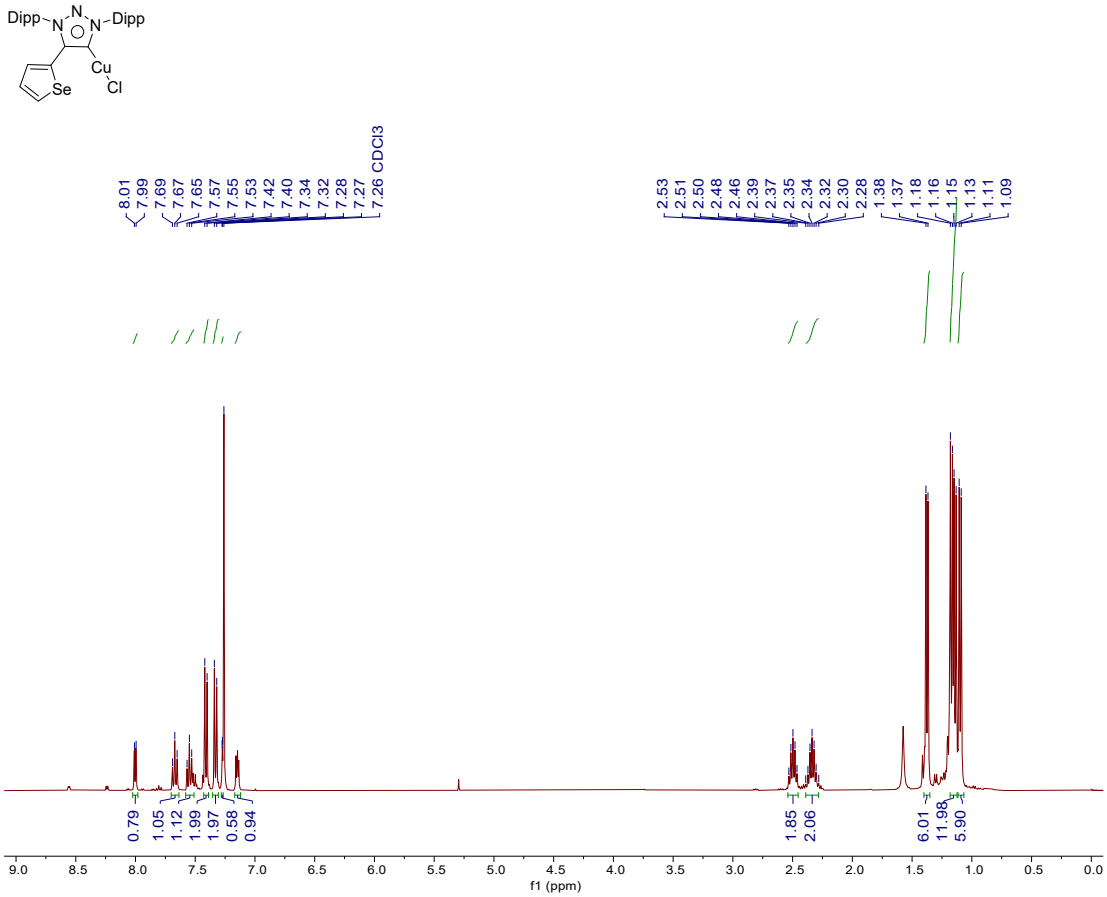


Figure S30:^{13}C-NMR spectrum of **10** in $CDCl_3$

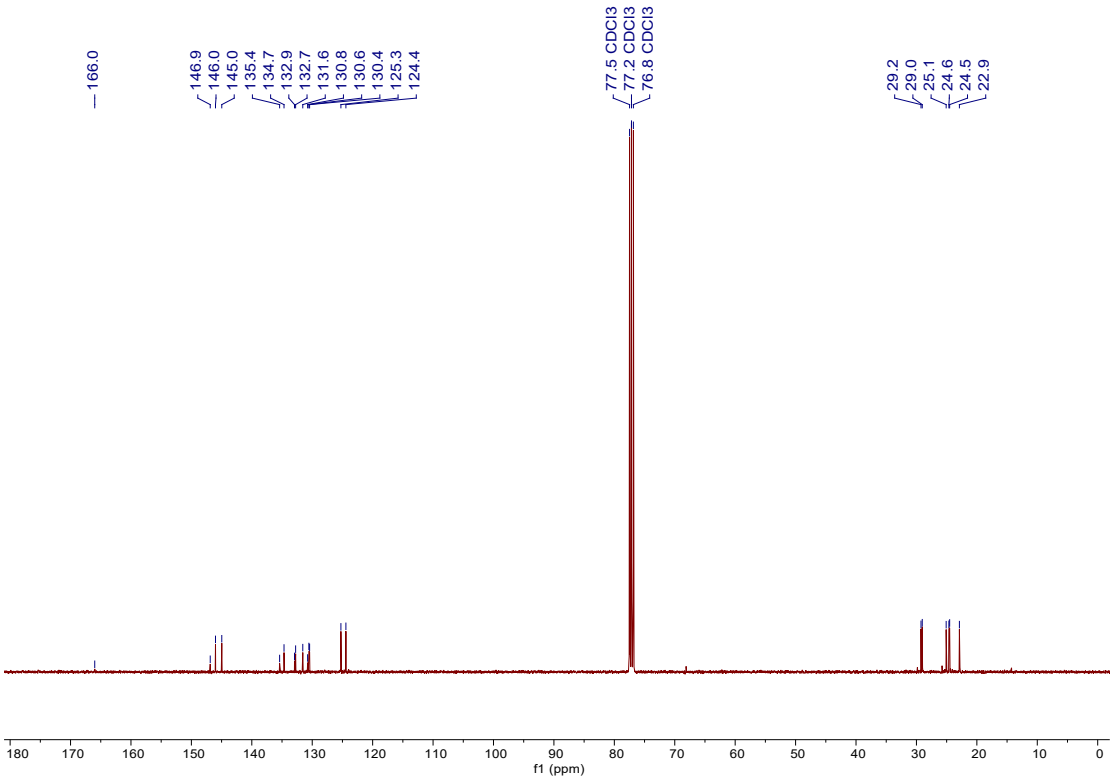


Figure S31:^{1}H-NMR spectrum of **4** in $CDCl_3$

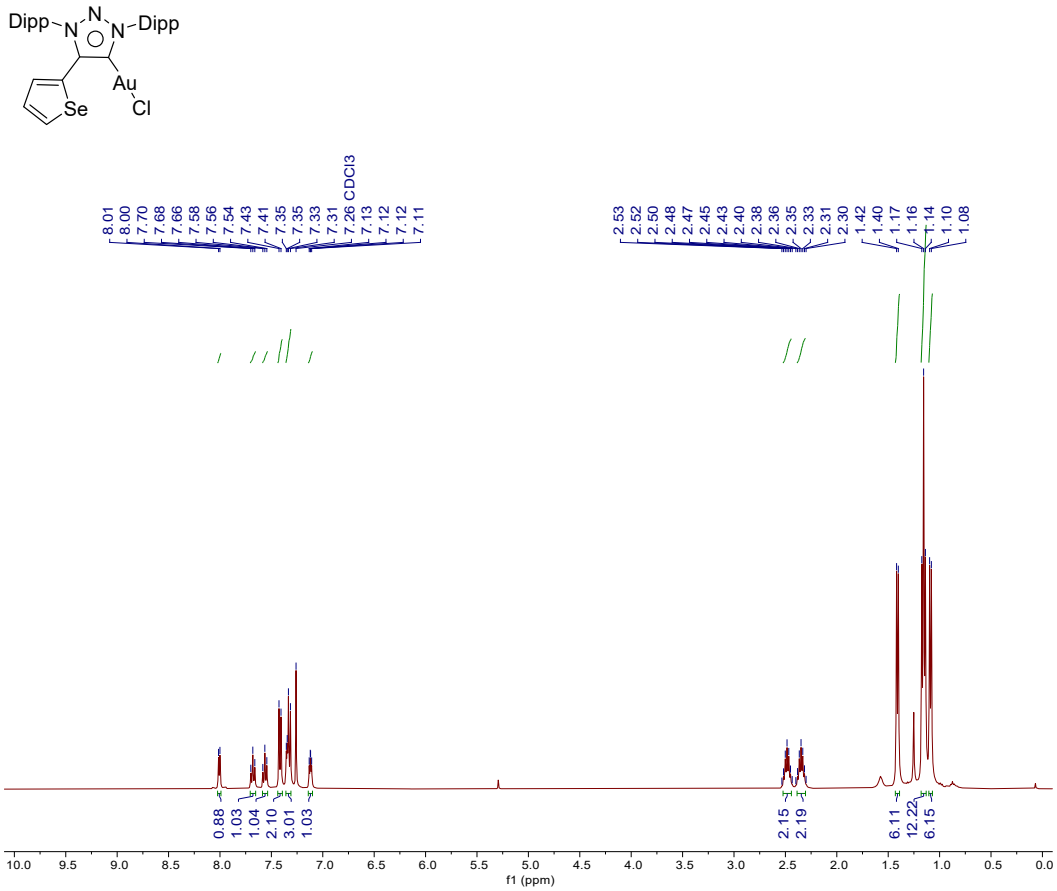


Figure S32:^{13}C-NMR spectrum of **4** in $CDCl_3$

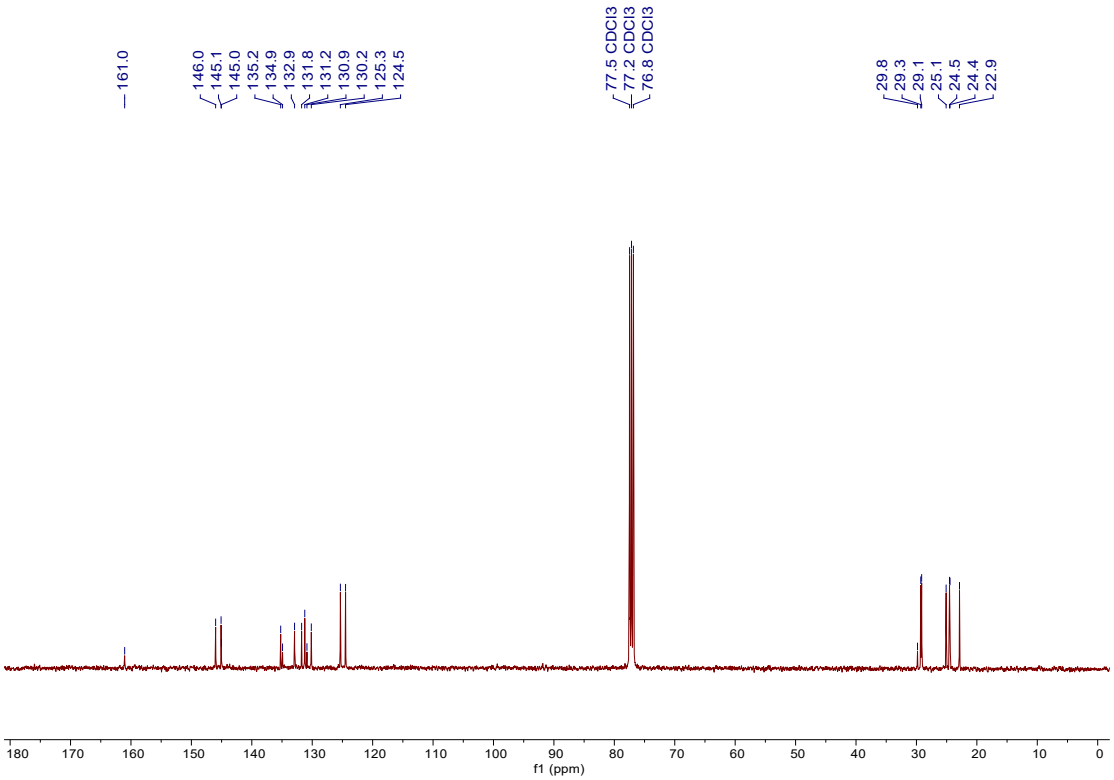


Figure S33:^{1}H-NMR spectrum of **L4-(H^{+})** in $CDCl_3$

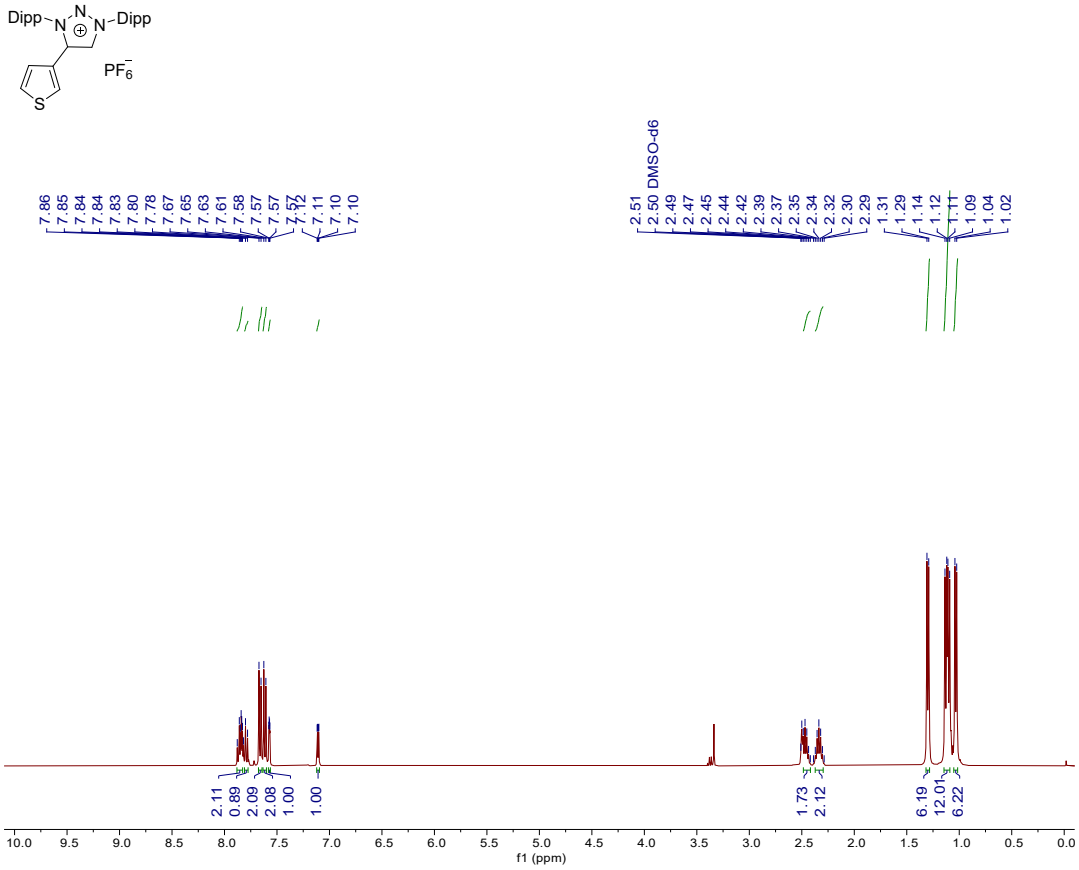


Figure S34:^{13}C-NMR spectrum of **L4-(H^{+})** in $CDCl_3$

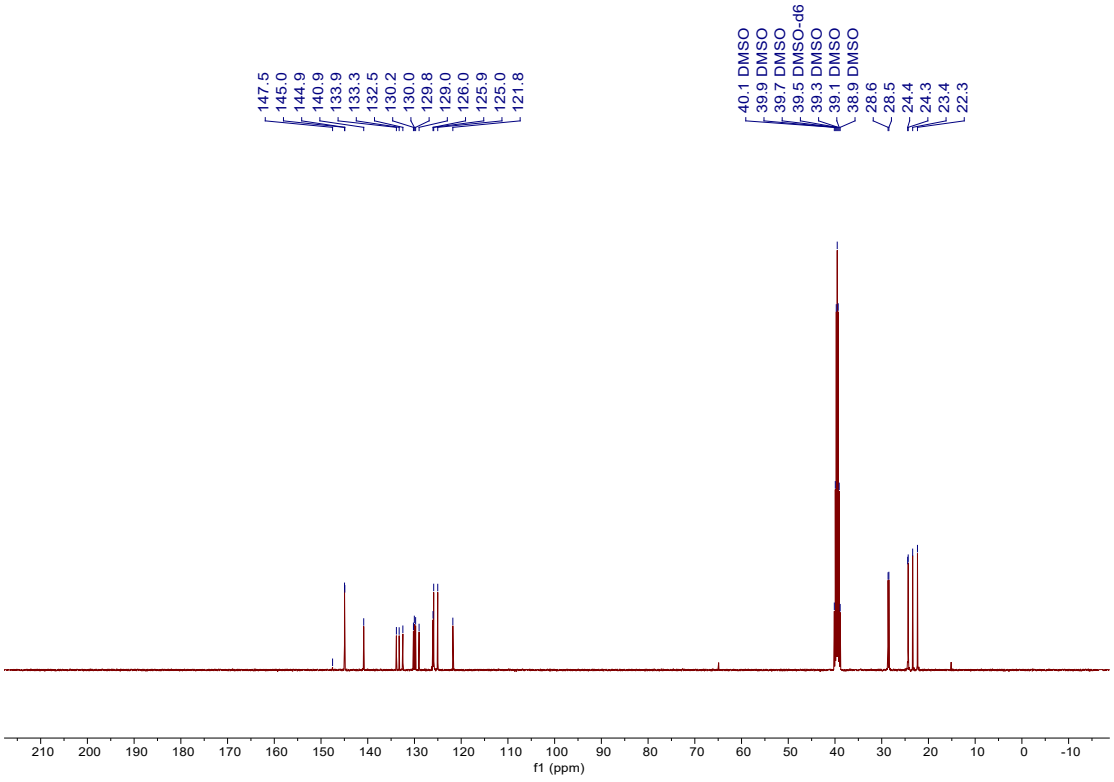


Figure S35:^{1}H-NMR spectrum of **11** in $CDCl_3$

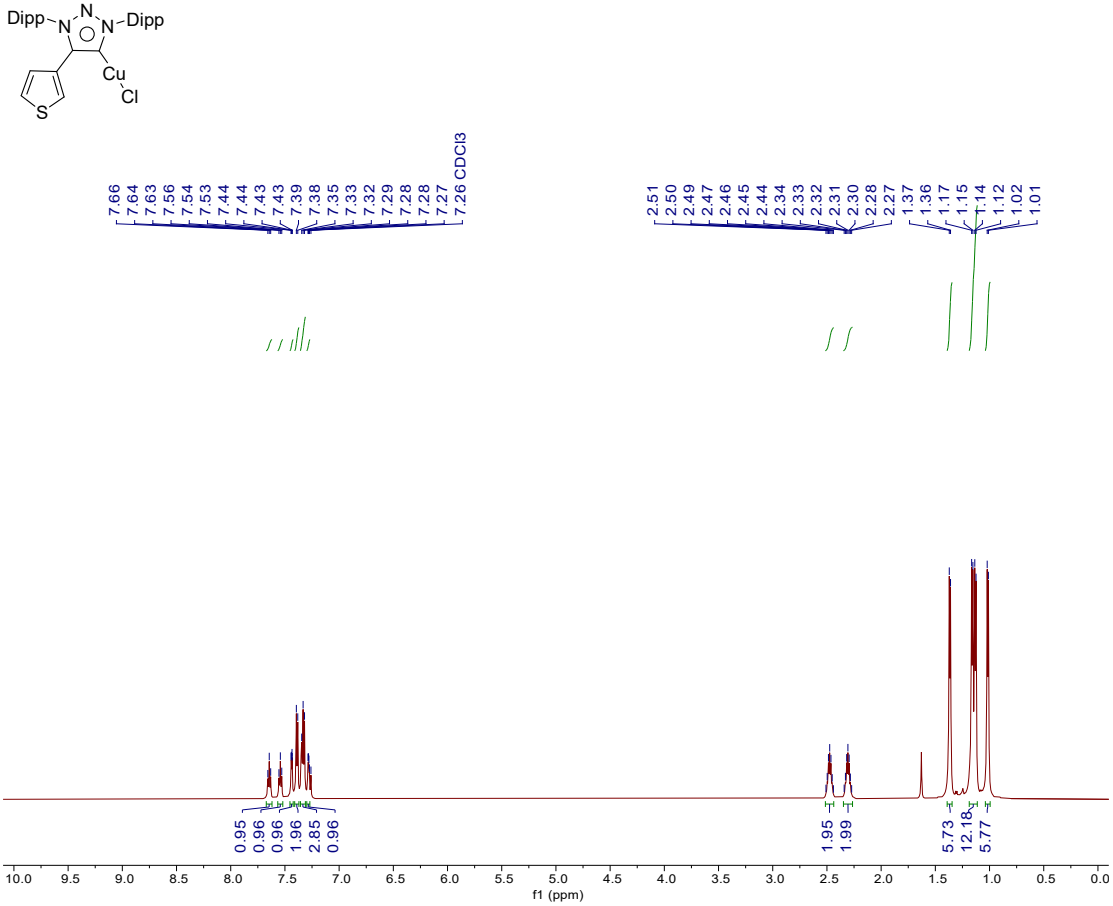


Figure S36:^{13}C-NMR spectrum of **11** in $CDCl_3$

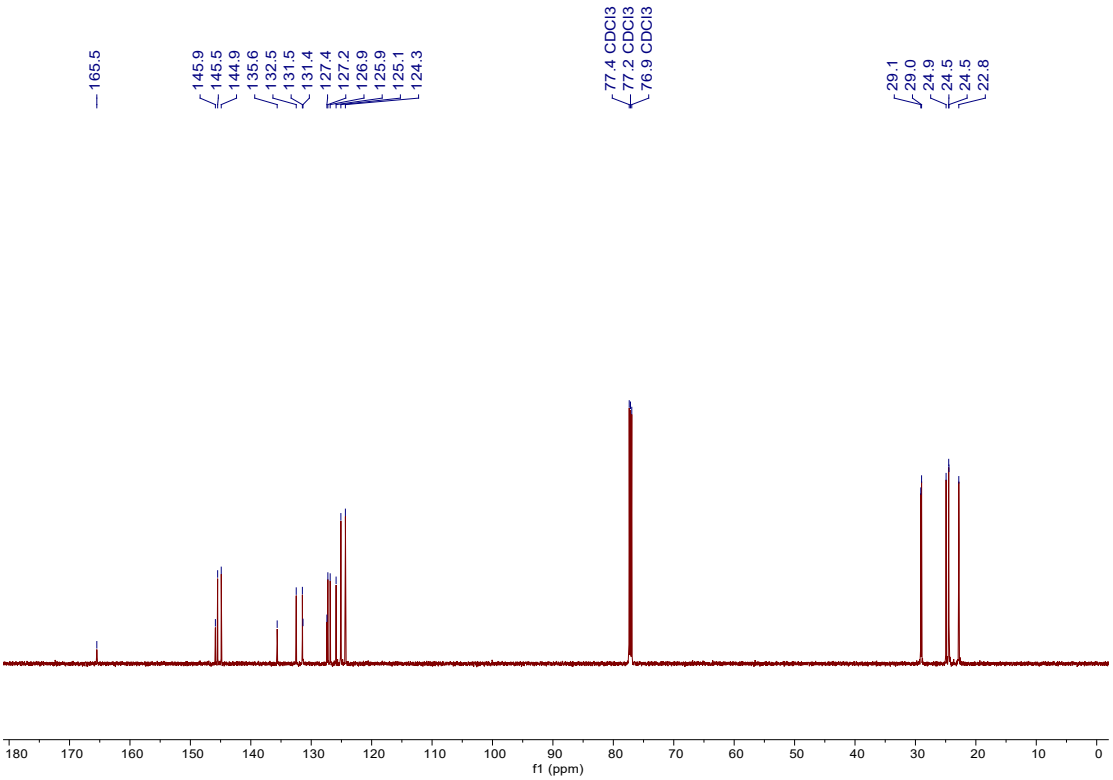


Figure S37:^{1}H-NMR spectrum of **5** in $CDCl_3$

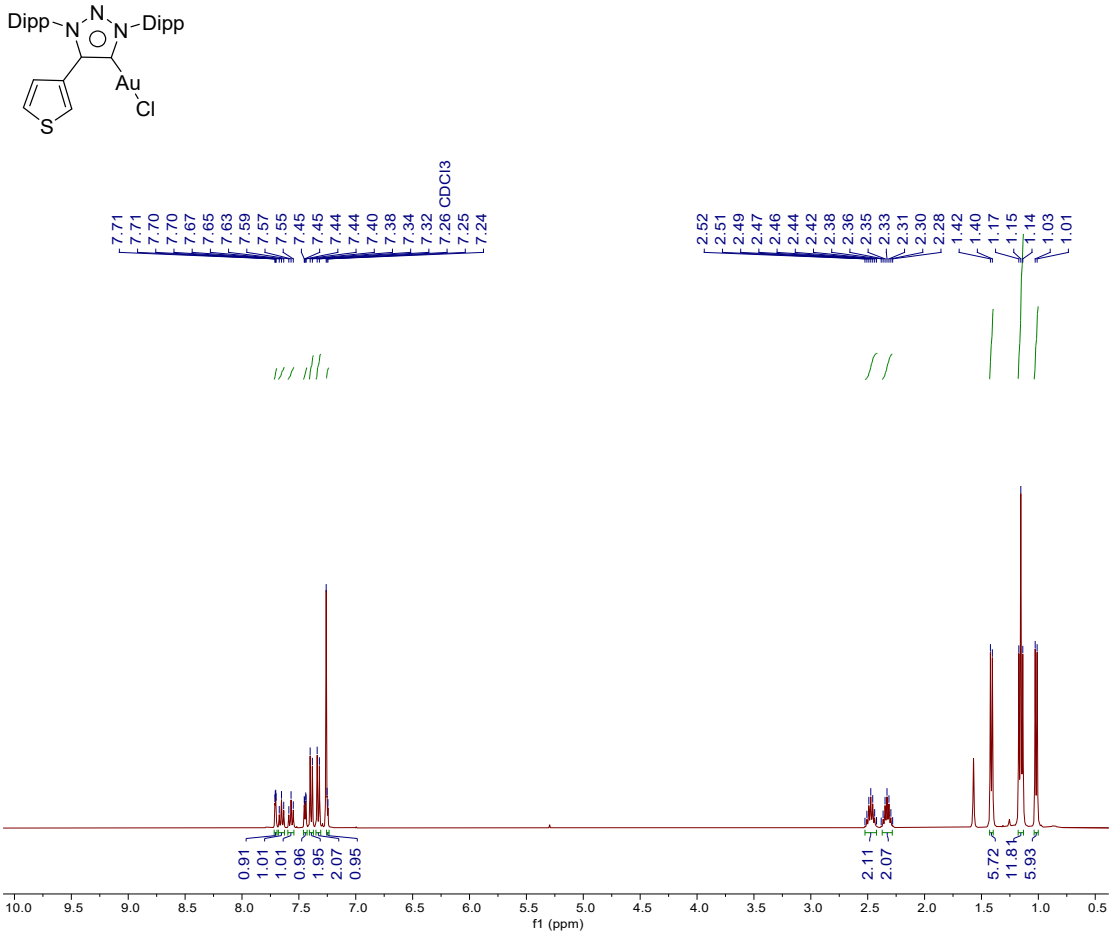


Figure S38:^{13}C-NMR spectrum of **5** in $CDCl_3$

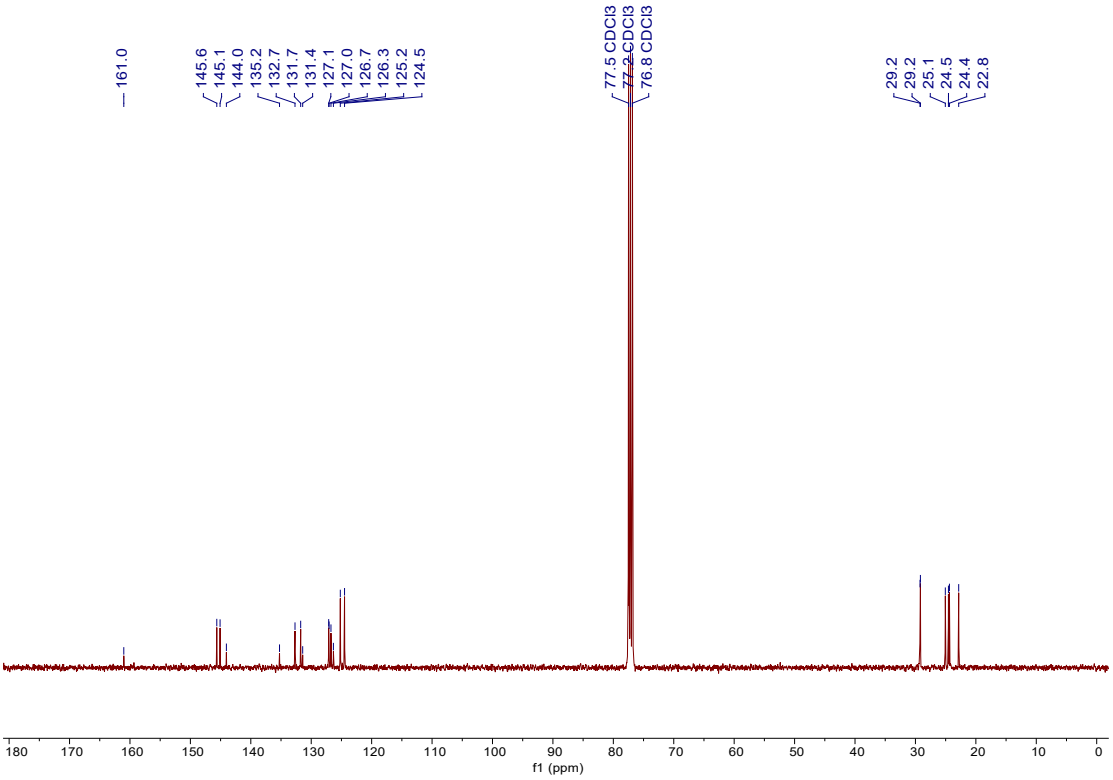


Figure S39:^{1}H-NMR spectrum of **6** in $CDCl_3$

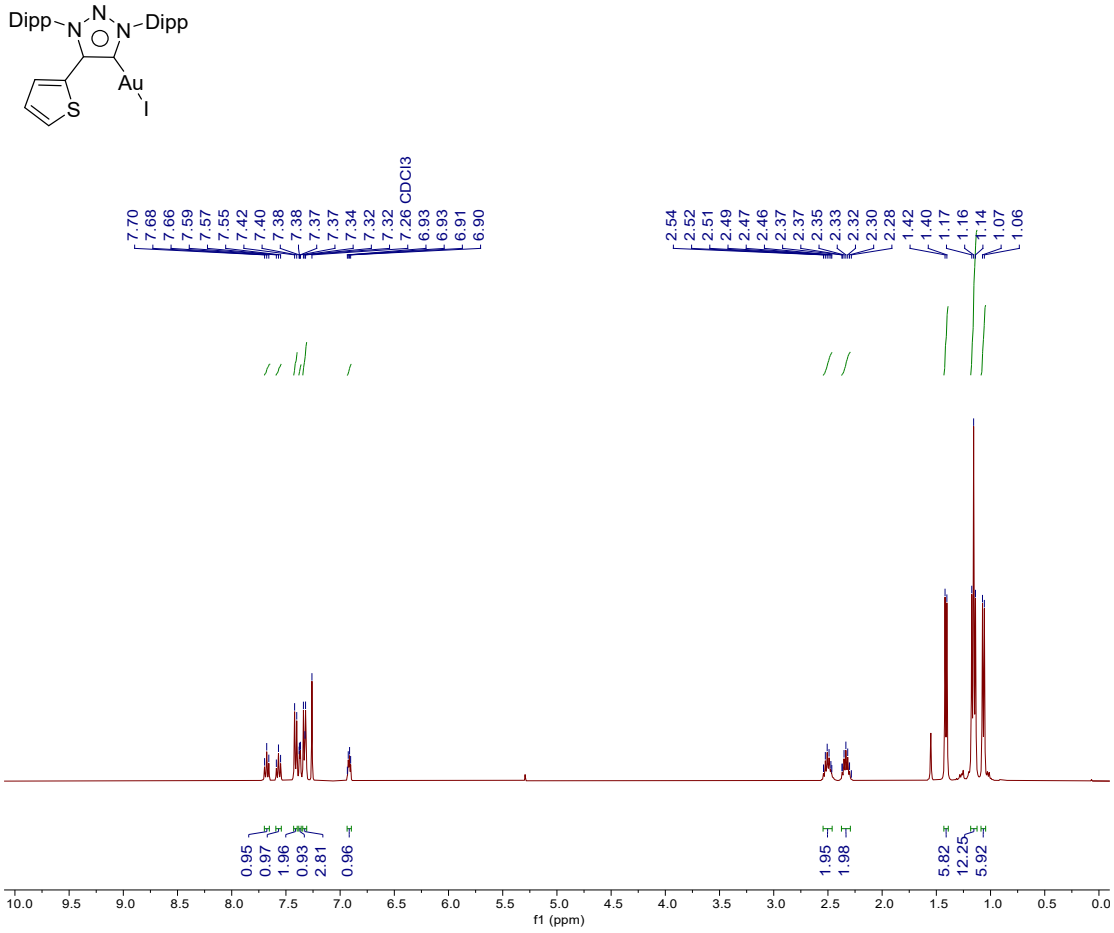


Figure S40:^{13}C-NMR spectrum of **6** in $CDCl_3$

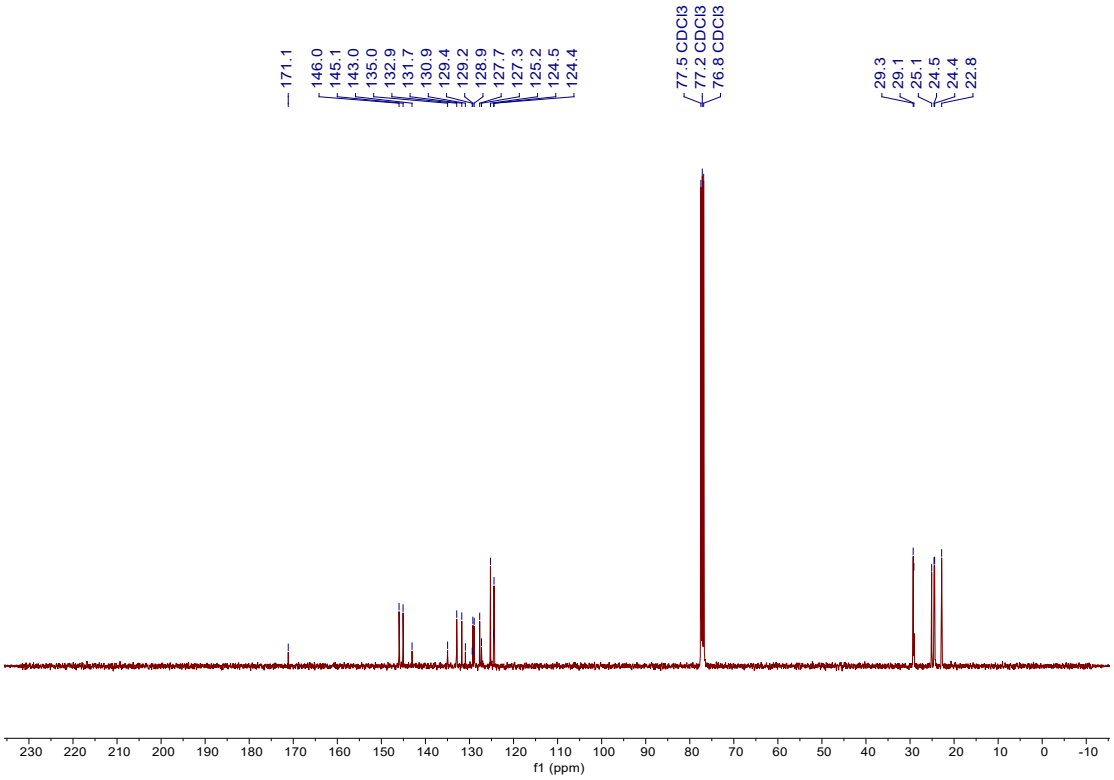


Figure S41:^{1}H-NMR spectrum of **7** in $CDCl_3$

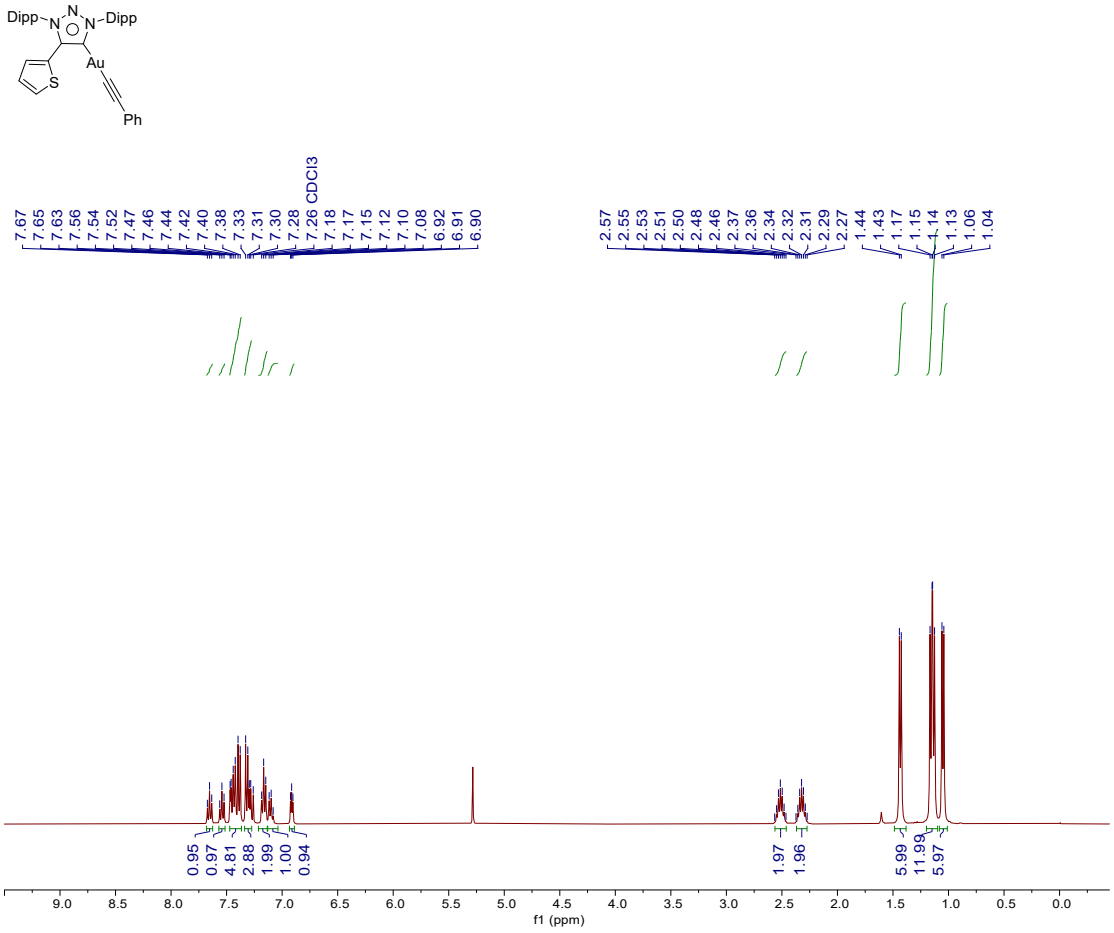


Figure S42:^{13}C-NMR spectrum of **7** in $CDCl_3$