Supporting Information

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1 General information

Practical considerations

Unless otherwise specified, all reactions were carried out in oven dried vials or reaction vessels with magnetic stirring under argon atmosphere. Screens were performed in 2.5 mL or 5.0 mL glass vials with a PTFE-lined cap, and all other reactions were performed in round-bottom flasks with rubber septa. All experiments were monitored by analytical thin layer chromatography (TLC). TLC was performed on pre-coated silica gel plates. After elution, plate was visualized under UV illumination at 254 nm for UV active materials. Solvents were removed in vacuo and heated with a water bath at 35 °C. Silica gel finer than 100-200 mesh was used for flash column chromatography. Columns were packed as slurry of silica gel in petroleum ether and equilibrated with the appropriate solvent mixture prior to use. The compounds were loaded neat or as a concentrated solution using the appropriate solvent system. The elution was assisted by applying pressure with an air pump.

Materials

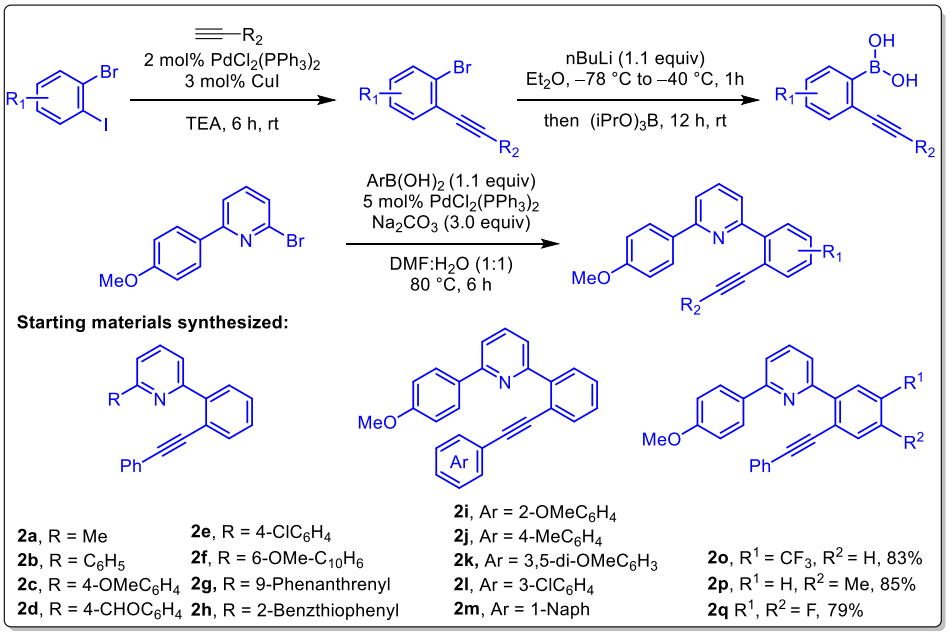
Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Anhydrous dichloromethane and acetonitrile were dried by using standard protocol under nitrogen. Gold, silver and phosphine ligands were purchased from Sigma-Aldrich. Deuterated solvents were used as supplied.

Instrumentation

NMR spectra were recorded on 400/500/700 MHz spectrometers in appropriate solvents using TMS as internal standard or the solvent signals as secondary standards and the chemical shifts are shown in δ scales. Multiplicities of ^{1}H NMR signals are designated as s (singlet), d (doublet), dd (doublet of doublet), dt (doublet of triplet), t (triplet), quin(quintet), m (multiplet) etc. HRMS data were recorded on a Bruker Daltonics MicroTOF-Q-II with Electron Spray Ionization (ESI). Single crystal X-ray 3 diffraction measurements were carried out on Bruker D8 Venture Dual source X-ray diffractometer and Bruker APEX-II CCD systems. Electrochemical measurements were performed CHI700E biopotentiostat workstation

2 Synthesis of pyridino-alkynes

General procedure for synthesis of pyridino-alkynes: All the starting material are reported and prepared according to literature known procedure.[1]



3 Synthesis of BQ-AuL complexes via aminoauration of pyridino-alkynes

Representative procedure: To a screw-cap vial containing a stir bar were added 2-methyl-6-(2-(phenylethynyl)phenyl)pyridine (**1a**) (30 mg, 0.11 mmol, 1.0 equiv), Ph_3PAuCl (**2a**) (54 mg, 1.0 equiv), AgOTf (28 mg, 1.0 equiv) and DCE (4 mL). The reaction vial was fitted with a cap, evacuated and back filled with N_2 and heated at 80 °C for 12 h. Upon completion of the reaction, the reaction mixture was allowed to cool to room temperature. Later, the it was diluted with CH_2Cl_2 (10 mL) and the combined mixture was concentrated in vacuo and the resulting residue was purified by column chromatography on silica (CH_2Cl_2/MeOH; 95:05) to afford the product **3a** in 68% yield. **Note:** All the reactions were performed at 0.11 mmol scale as mentioned in the representative procedure.

[1] Mule, R. D.; Shaikh, A. C.; Gade, A. B.; Patil, N. T. *Chem. Commun*., **2018**, *54*, 11909

4 Phase-wise synthesis of BQ-AuL complexes and their characterization data

The synthesis and screening of 40 Benzo[*a*]quinolizinium (BQ)-based Au complexes for their anticancer activity and ATP secretion was performed in three phases as mentioned below. All the synthesized complexes were characterized unambeguously by ^{1}H, ^{13}C, ^{19}F, ^{31}P, ^{11}B NMR and HRMS. Please refer to Section 8 for the anticancer activity and ATP secretion studies.

Phase 1: Considering the significant effect of the nature and type of ligands, on the stability and reactivity of gold complexes, we began our study by analyzing the effect of substitution on the BQ skeleton in BQ-AuL complexes on their biological properties. To this end, we synthesized 17 variably functionalized BQ-AuPPh$_3$ (**3a-3q**) complexes as given in **Figure S4.1**. Upon screening, complex **3c** was identified as the best BQ skeleton on the basis of its IC_{50} value and ability to induce ATP secretion (*cf.* Section 8).

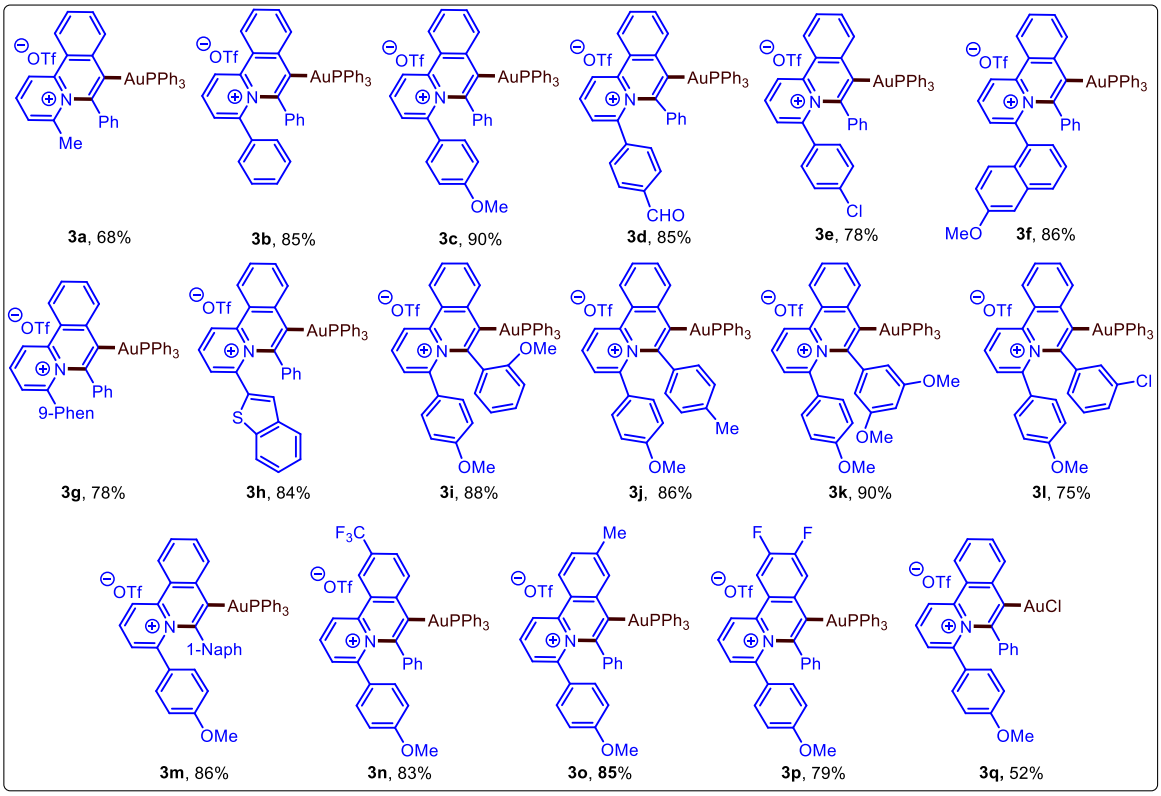


Figure S4.1. Synthesis of 17 BQ-AuPPh$_3$ complexes bearing diverse substitution in BQ skeleton.

Phase 2: We then focused our attention towards the screening of various ligands on gold complex. In this regard, we synthesized 17 different variants of BQ-AuL containing different

phosphine- (**4a-4h**) and NHC-based ligands (**4i-4q**), as given in **Figure S4.2**. The IC_{50} and ATP release ability of **4k** was found to be the best among all the synthesized compounds (*cf.* Section 8).

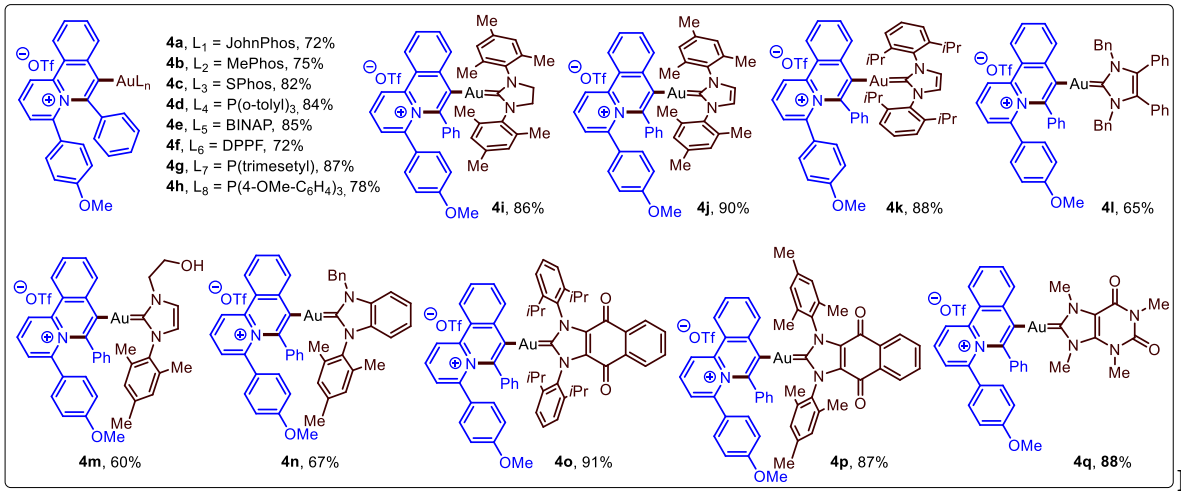


Figure S4.2. Synthesis of 17 BQ-AuPPh$_3$ complexes bearing diverse substitution in BQ skeleton.

Phase 3: After identifying the most effective substitution on BQ and the right ligand (L) in BQ-AuL complexes (**4k**), we focused our study analyzing the effect of variation in counter-anion in **4k**. Moreover, for some other complexes with variation in BQ skeleton of BQ-AuIPr were also synthesized (**5a-5f**).

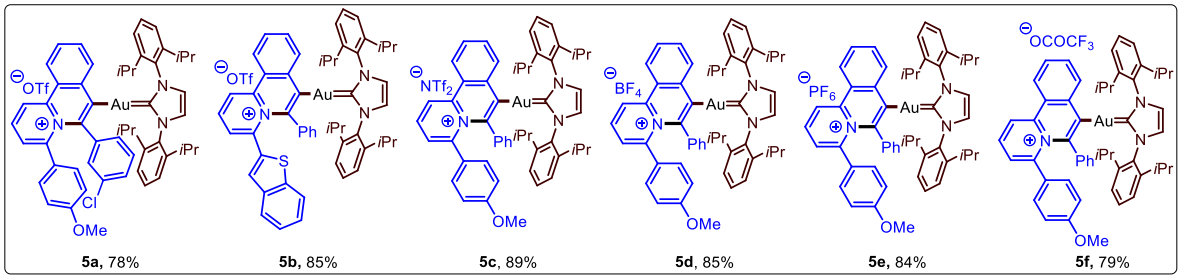
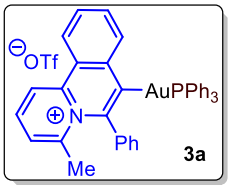
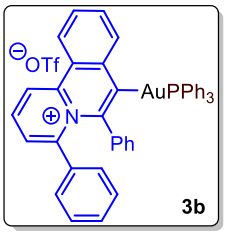


Figure S4.3. Synthesis of different counter anion bearing **4k** complexes and other BQ-AuIPr complexes.

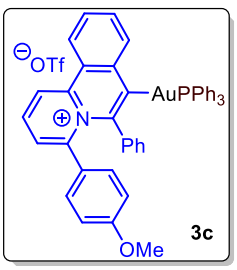


(**3a**): Pale yellow solid, 68 mg, 70% yield; R_f = 0.50 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (500 MHz, DMSO-d$_6$) δ** = 9.43 (d, *J* = 8.1 Hz, 1 H), 9.11 (d, *J* = 8.5 Hz, 1 H), 8.75 - 8.64 (m, 1

H), 8.49 (dd, *J* = 7.5, 8.5 Hz, 1 H), 8.14 - 8.07 (m, 1 H), 7.98 - 7.92 (m, 1 H), 7.90 (d, *J* = 7.0 Hz, 1 H), 7.76 - 7.70 (m, 2 H), 7.66 - 7.62 (m, 3 H), 7.61 - 7.56 (m, 6 H), 7.46 - 7.38 (m, 7 H), 7.36 - 7.31 (m, 2 H), 2.15 (s, 3 H); **^{13}C NMR (125 MHz, DMSO-d$_6$) δ** = 173.1 (d, J_{C-P} = 108 Hz), 148.0, 145.9, 143.2, 142.7 (d, J_{C-P} = 5 Hz), 139.4, 138.0, 133.7 (d, J_{C-P} = 14 Hz), 133.6, 132.7, 131.9, 129.5 (d, J_{C-P} = 11 Hz), 129.4, 129.1, 129.0, 128.8, 128.5, 127.8, 125.3, 124.5 121.9, 120.7 (q, J_{C-F} = 322.7 Hz), 26.1; **^{19}F NMR (375 MHz, DMSO-d$_6$) δ** = –77.73; **^{31}P NMR (162 MHz, DMSO-d$_6$) δ** = 41.20; **HRMS (ESI)** calcd for $C_{38}H_{30}AuPN^+$ (M - OTf)$^+$ 728.1812, found 728.1815.

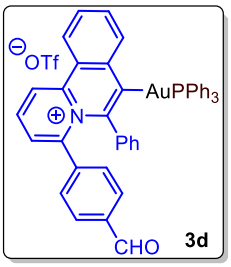


(**3b**): Yellow solid, 87 mg, 85% yield; ***R$_f$*** = 0.30 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (500 MHz, DMSO-d$_6$) δ** = 9.48 (d, *J* = 7.8 Hz, 1 H), 9.15 (d, *J* = 8.4 Hz, 1 H), 8.66 (d, *J* = 7.9 Hz, 1 H), 8.56 (dd, *J* = 7.5, 8.4 Hz, 1 H), 8.12 (t, *J* = 7.6 Hz, 1 H), 7.97 (t, *J* = 7.2 Hz, 1 H), 7.91 - 7.83 (m, 1 H), 7.63 - 7.57 (m, 3 H), 7.56 - 7.49 (m, 6 H), 7.30 -7.34 (m, 6 H), 7.28 - 7.23 (m, 1 H), 7.20 (t, *J* = 7.4 Hz, 2 H), 7.15 - 7.12 (m, *J* = 7.2 Hz, 2 H), 7.12 - 7.08 (m, *J* = 7.2 Hz, 2 H), 7.04 (t, *J* = 7.5 Hz, 1 H), 6.90 (t, *J* = 7.6 Hz, 2 H); **^{13}C NMR (125 MHz, DMSO-d$_6$) δ** = 172.1 (d, J_{C-P} = 109.9 Hz), 149.4, 146.8, 144.3 (d, J_{C-P} = 5.4 Hz) , 143.4, 140.4, 137.7 (d, J_{C-P} = 40.8 Hz), 133.6 (d, J_{C-P} = 13.6 Hz), 133.0, 131.8, 129.4 (d, J_{C-P} = 10.9 Hz), 129.4, 129.2, 129.0, 128.9, 128.5, 128.1, 127.6, 127.1, 125.6, 124.2, 124.1, 121.7; **^{19}F NMR (375 MHz, DMSO-d$_6$) δ** = –77.75; **^{31}P NMR (162 MHz, DMSO-d$_6$) δ** = 41.11; **HRMS (ESI)** calcd for $C_{43}H_{32}AuPN^+$ (M - OTf)$^+$ 790.1940, found 790.1930.

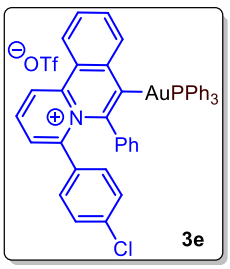


(**3c**): Yellow solid, 96 mg, 90% yield; ***R$_f$*** = 0.30 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (500 MHz, DMSO-d$_6$) δ** = 9.42 (d, *J* = 7.8 Hz, 1 H), 9.12 (d, *J* = 8.4 Hz, 1 H), 8.64 (d, *J* = 7.6 Hz,

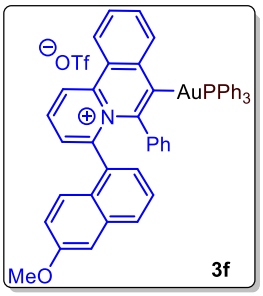
1 H), 8.56 - 8.49 (m, 1 H), 8.10 (t, *J* = 7.6 Hz, 1 H), 7.99 - 7.92 (m, 1 H), 7.87 - 7.81 (m, 1 H), 7.61 - 7.58 (m, 3 H), 7.54 (dt, *J* = 1.8, 7.5 Hz, 6 H), 7.31 – 7.35 (m, 6 H), 7.14 (d, *J* = 7.2 Hz, 2 H), 7.07 - 7.05 (m, 3 H), 6.96 - 6.93 (m, 2 H), 6.75 (d, *J* = 8.9 Hz, 2 H), 3.73 (s, 3 H); **^{13}C NMR (125 MHz, DMSO-d$_6$) δ** = 171.7 (d, $J_{C\text{-}P}$ = 108.1 Hz), 160.1, 149.7, 146.8, 144.4, 143.5, 140.3, 138.0, 133.7 (d, $J_{C\text{-}P}$ = 13.6 Hz), 133.4, 132.9, 131.8, 130.3, 129.4 (d, $J_{C\text{-}P}$ = 10.9 Hz), 129.3, 129.0, 128.6, 128.0, 127.4, 127.1, 125.5, 124.1, 121.3, 120.9, 120.7 (d, $J_{C\text{-}F}$ = 322.7 Hz), 114.1, 55.4; **^{19}F NMR (375 MHz**, **DMSO-d$_6$) δ** = –77.71; **^{31}P NMR (162 MHz**, **DMSO-d$_6$) δ** = 41.17; **HRMS (ESI)** calcd for $C_{44}H_{34}AuPON^+$ (M - OTf)$^+$ 820.2014, found 820.2005.



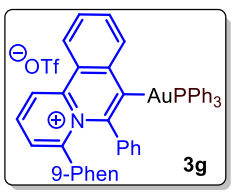
(3d): Yellow solid, 90.5 mg, 85% yield; ***R$_f$*** = 0.30 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR** (**400 MHz ,DMSO-d$_6$**) **δ** = 9.96 (s, 1 H), 9.54 (d, *J* = 8.3 Hz, 1 H), 9.19 (d, *J* = 8.4 Hz, 1 H), 8.69 (d, *J* = 7.9 Hz, 1 H), 8.58 (t, *J* = 7.9 Hz, 1 H), 8.14 (t, *J* = 7.5 Hz, 1 H), 8.00 (t, *J* = 7.6 Hz, 1 H), 7.93 (d, *J* = 7.1 Hz, 1 H), 7.72 (d, *J* = 8.2 Hz, 2 H), 7.62 - 7.56 (m, 3 H), 7.56 - 7.48 (m, 6 H), 7.26 - 7.38 (m, 8 H), 7.20 (d, *J* = 7.3 Hz, 2 H), 7.06 (t, *J* = 7.4 Hz, 1 H), 6.91 (t, *J* = 7.6 Hz, 2 H); **^{13}C NMR** (**100 MHz ,DMSO-d$_6$**) **δ** = 192.6, 172.7 (d, $J_{C\text{-}P}$ = 109.3 Hz), 147.8, 146.9, 144.2 (d, $J_{C\text{-}P}$ = 4.5 Hz) 143.2, 143.2, 142.6, 140.7, 137.8, 135.6, 133.7, 133.7 (d, $J_{C\text{-}P}$ = 13.9 Hz), 133.2, 131.8, 129.5, 129.5 (d, $J_{C\text{-}P}$ = 11.7 Hz), 129.4, 128.9, 128.5, 128.3, 127.6, 127.4, 125.7, 124.2, 122.5; **^{19}F NMR** (**375 MHz ,DMSO-d$_6$**) **δ** = –77.74; **HRMS (ESI)** calcd for $C_{44}H_{32}AuPON^+$ (M - OTf)$^+$ 818.1882, found 818.1919



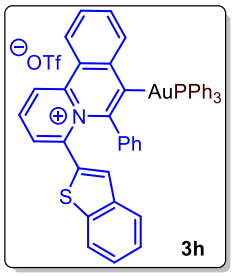
(3e): Yellow solid, 83.5 mg, 78% yield; ***Rf*** **=** 0.40 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (500 MHz, DMSO-d$_6$) δ** = 9.56 - 9.43 (m, 1 H), 9.16 (d, *J* = 8.4 Hz, 1 H), 8.67 (d, *J* = 7.6 Hz, 1 H), 8.56 (dd, *J* = 7.4, 8.5 Hz, 1 H), 8.12 (t, *J* = 7.6 Hz, 1 H), 8.02 - 7.93 (m, 1 H), 7.88 (dd, *J* = 1.1, 7.3 Hz, 1 H), 7.64 - 7.58 (m, 3 H), 7.58 - 7.52 (m, 7 H), 7.38 (br. s., 5 H), 7.28 - 7.24 (m, *J* = 8.5 Hz, 2 H), 7.19 (d, *J* = 7.2 Hz, 2 H), 7.16 - 7.12 (m, *J* = 8.5 Hz, 2 H), 7.12 - 7.07 (m, 1 H), 7.01 - 6.93 (m, 2 H); **^{13}C NMR (125 MHz, DMSO-d$_6$) δ** = 148.0, 146.9, 144.1, 143.4, 140.5, 137.9, 136.3, 134.0, 133.7 (d, $J_{C\text{-}P}$ = 13.6 Hz), 133.7, 133.1, 131.9, 129.5 (d, $J_{C\text{-}P}$ = 10 Hz), 129.5, 129.3, 129.1, 128.9, 128.5, 128.1, 127.6, 127.4, 125.6, 124.2, 122.1, 120.7 (d, $J_{C\text{-}F}$ = 322.4 Hz); **^{19}F NMR (375 MHz, DMSO-d$_6$) δ** = –77.73; **^{31}P NMR (162 MHz, DMSO-d$_6$) δ** = 41.01; **HRMS (ESI)** calcd for $C_{43}H_{31}AuClPN^+$ $(M - OTf)^+$ 824.1554, found 824.1559.



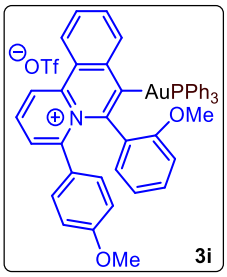
(3f): Yellow solid, 96 mg, 86% yield; ***Rf*** **=** 0.30 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (500 MHz, DMSO-d$_6$) δ** = 9.48 (dd, *J* = 1.1, 8.8 Hz, 1 H), 9.16 (d, *J* = 8.5 Hz, 1 H), 8.71 - 8.63 (m, 1 H), 8.58 (dd, *J* = 7.4, 8.5 Hz, 1 H), 8.17 - 8.07 (m, 1 H), 8.05 - 7.93 (m, 2 H), 7.70 (d, *J* = 9.0 Hz, 1 H), 7.65 - 7.60 (m, 2 H), 7.59 - 7.54 (m, 3 H), 7.54 - 7.46 (m, 6 H), 7.37 - 7.24 (m, 7 H), 7.21 (d, *J* = 7.5 Hz, 1 H), 7.18 - 7.12 (m, 2 H), 7.03 (d, *J* = 7.6 Hz, 1 H), 6.90 - 6.81 (m, 1 H), 6.72 (q, *J* = 7.8 Hz, 2 H), 3.88 (s, 3 H); **^{13}C NMR (125 MHz, DMSO-d$_6$) δ** = 172.2 (d, $J_{C\text{-}P}$ = 109 Hz), 158.4, 149.8, 146.8, 144.4 (d, $J_{C\text{-}P}$ = 4.5 Hz), 143.3, 140.5, 137.9, 134.2, 133.6 (d, $J_{C\text{-}P}$ = 13.6 Hz), 133.0, 132.7, 131.8, 129.9, (d, $J_{C\text{-}P}$ = 10.9 Hz), 129.4, 129.0, 128.7, 128.6, 127.9, 127.8, 127.7, 127.6, 127.4, 127.1, 127.0, 125.6, 125.1, 124.1 (d, $J_{C\text{-}P}$ = 3.6 Hz), 121.5, 120.7 (d, $J_{C\text{-}F}$ = 321.5 Hz), 119.3, 105.8, 55.3; **^{19}F NMR (375 MHz, DMSO-d$_6$) δ** = –77.73; **^{31}P NMR (162 MHz, DMSO-d$_6$) δ** = 41.12; **HRMS (ESI)** calcd for $C_{48}H_{36}AuPON^+$ $(M - OTf)^+$ 870.2245, found 870.2259.



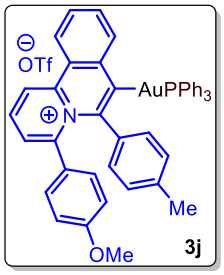
(3g): Yellow solid, 89 mg, 78% yield; ***Rf*** **=** 0.30 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (400MHz ,DMSO-d$_6$) δ** = 9.68 (d, *J* = 8.1 Hz, 1 H), 9.26 (d, *J* = 8.4 Hz, 1 H), 8.77 (d, *J* = 8.3 Hz, 2 H), 8.71 - 8.63 (m, 2 H), 8.21 - 8.11 (m, 2 H), 8.03 (t, *J* = 7.6 Hz, 1 H), 7.84 (d, *J* = 7.6 Hz, 1 H), 7.79 - 7.73 (m, 1 H), 7.73 - 7.62 (m, 5 H), 7.57 - 7.51 (m, 3 H), 7.45 (t, *J* = 6.1 Hz, 6 H), 7.31 (d, *J* = 8.1 Hz, 1 H), 7.15 - 7.21 (m, 5 H), 6.96 - 6.86 (m, 1 H), 6.66 (d, *J* = 7.6 Hz, 1 H), 6.44 - 6.32 (m, 2 H), 6.31 - 6.16 (m, 1 H); **^{13}C NMR (175 MHz, DMSO-d$_6$) δ** = 172.9 (d, $J_{C\text{-}P}$ = 109.3 Hz), 147.1, 146.4, 144.2 (d, $J_{C\text{-}P}$ = 3.8 Hz), 142.0, 140.0, 137.6, 133.7, 133.5 (d, $J_{C\text{-}P}$ = 14 Hz), 133.1, 133.0, 131.8, 130.1, 129.9, 129.8, 129.6 (d, $J_{C\text{-}P}$ = 5 Hz), 129.5, 129.4, 129.4 (d, $J_{C\text{-}P}$ = 10.2 Hz), 129.1, 129.0, 128.4, 128.1, 127.3, 127.2, 127.2, 127.0, 127.0, 126.8, 126.3, 125.7, 124.8, 124.5 (d, $J_{C\text{-}P}$ = 3.8 Hz), 123.3, 122.8, 122.7, 120.7 (q, $J_{C\text{-}F}$ = 321.7 Hz); **^{19}F NMR (375 MHz**, **DMSO-d$_6$) δ** = –77.73; **^{31}P NMR (162 MHz**, **DMSO-d$_6$) δ** = 40.67; **HRMS (ESI)** calcd for $C_{51}H_{36}AuNP$ $(M - OTf)^+$ 890.2245, found 890.2248.



(3h): Yellow solid, 88 mg, 84% yield; ***Rf*** **=** 0.40 (CH_2Cl_2/MeOH = 96/04); **^{1}H NMR (500 MHz**, **DMSO-d$_6$) δ** = 9.52 (d, *J* = 8.9 Hz, 1 H), 9.15 (d, *J* = 8.5 Hz, 1 H), 8.69 (d, *J* = 7.9 Hz, 1 H), 8.61 - 8.51 (m, 1 H), 8.14 (t, *J* = 7.6 Hz, 1 H), 8.11 - 8.05 (m, 1 H), 8.02 - 7.95 (m, 1 H), 7.92 - 7.87 (m, 1 H), 7.80 - 7.74 (m, 1 H), 7.62 - 7.57 (m, 3 H), 7.55 - 7.48 (m, 6 H), 7.41 - 7.27 (m, 11 H), 6.96 (t, *J* = 7.4 Hz, 1 H), 6.80 (t, *J* = 7.8 Hz, 2 H); **^{13}C NMR (125 MHz**, **DMSO-d$_6$) δ** = 172.7 (d, $J_{C\text{-}P}$ = 109.9 Hz), 147.2, 144.5, 142.7, 140.7, 140.1, 138.5, 137.8, 137.5, 133.6 (d, $J_{C\text{-}P}$ = 13.6 Hz), 133.3, 131.9, 129.5 (d, $J_{C\text{-}P}$ = 10.9 Hz), 129.0, 128.6, 128.0, 127.5, 127.3, 125.9, 125.7, 125.0, 124.8, 124.1, 122.7, 122.4, 122.7, 120.7 (d, $J_{C\text{-}F}$ = 322.5 Hz); **^{19}F NMR (375 MHz**, **DMSO-d$_6$) δ** = –73.77; **^{31}P NMR (162 MHz**, **DMSO-d$_6$) δ** = 41.09; **HRMS (ESI)** calcd for $C_{45}H_{32}AuPSN^+$ $(M - OTf)^+$ 846.1788, found 846.1795.

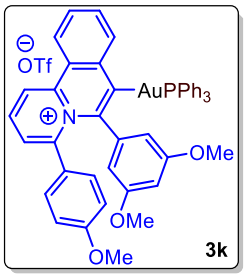


(3i): Yellow solid, 97 mg, 88% yield; ***Rf*** **=** 0.30 (CH_2Cl_2/MeOH = 93/07); **^{1}H NMR (500 MHz, DMSO-d$_6$) δ** = 9.48 - 9.40 (m, 1 H), 9.11 (d, *J* = 8.4 Hz, 1 H), 8.64 (d, *J* = 7.8 Hz, 1 H), 8.58 - 8.49 (m, 1 H), 8.09 (t, *J* = 7.3 Hz, 1 H), 8.00 - 7.93 (m, 1 H), 7.88 (dd, *J* = 1.1, 7.3 Hz, 1 H), 7.65 - 7.57 (m, 3 H), 7.57 - 7.48 (m, 6 H), 7.39 - 7.28 (m, 7 H), 7.13 - 7.06 (m, 2 H), 7.04 (dd, *J* = 2.3, 8.5 Hz, 1 H), 6.79 (dd, *J* = 2.6, 8.5 Hz, 1 H), 6.75 - 6.66 (m, 2 H), 6.44 (t, *J* = 7.4 Hz, 1 H), 3.72 (s, 3 H), 3.34 (s, 3 H); **^{13}C NMR (125 MHz, DMSO-d$_6$) δ** = 172.7, 160.5, 155.2, 149.8, 145.9, 140.5 (d, $J_{C\text{-}P}$ = 3.6 Hz), 137.9, 134.0 (d, $J_{C\text{-}P}$ = 13.6 Hz), 133.7, 133.2, 132.2, 131.1, 129.9, 129.8, 129.8 (d, $J_{C\text{-}P}$ = 10.9 Hz), 129.5 (d, $J_{C\text{-}P}$ = 10 Hz), 129.4, 127.5, 125.8, 124.1, 122.8, 121.5, 120.6, 119.3, 114.6, 114.2, 110.5, 55.7, 55.4; **^{19}F NMR (365 MHz, DMSO-d$_6$) δ** = –77.78; **^{31}P NMR (162 MHz, DMSO-d$_6$) δ** = 40.92; **HRMS (ESI)** calcd for $C_{45}H_{36}AuO_2PN^+$ $(M - OTf)^+$ 850.2114, found 850.2116.

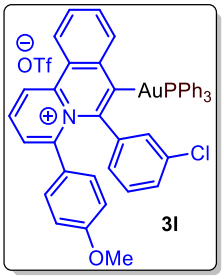


(3j): Yellow solid, 93 mg, 86% yield; ***Rf*** **=** 0.30 (CH_2Cl_2/MeOH = 93/07); **^{1}H NMR (700 MHz ,DMSO-d$_6$) δ** = 9.40 (d, *J* = 8.6 Hz, 1 H), 9.10 (d, *J* = 8.2 Hz, 1 H), 8.63 (d, *J* = 8.0 Hz, 1 H), 8.51 (t, *J* = 7.7 Hz, 1 H), 8.09 (t, *J* = 7.4 Hz, 1 H), 7.94 (t, *J* = 7.5 Hz, 1 H), 7.83 (d, *J* = 7.3 Hz, 1 H), 7.68 - 7.59 (m, 4 H), 7.54 (br. s., 6 H), 7.34 (br. s., 5 H), 7.02 (d, *J* = 7.7 Hz, 2 H), 7.01 - 6.95 (m, *J* = 7.3 Hz, 2 H), 6.77 - 6.73 (m, *J* = 7.7 Hz, 2 H), 6.71 (d, *J* = 7.3 Hz, 2 H), 3.73 (s, 3 H), 2.11 (s, 3 H); **^{13}C NMR (175 MHz, DMSO-d$_6$) δ** = 160.1, 149.7, 146.8, 144.6, 140.7, 140.4, 137.8, 136.5, 133.7 (d, $J_{C\text{-}P}$ = 12.7 Hz), 133.5, 132.9, 131.9, 130.4, 129.5 (d, $J_{C\text{-}P}$ = 8.9 Hz), 129.3, 129.2 (d, $J_{C\text{-}P}$ = 6.2 Hz), 128.6, 128.5, 127.3, 125.5, 124.1, 120.7 (d, $J_{C\text{-}F}$ = 322.9 Hz), 120.2, 113.9, 55.5, 20.8; **^{19}F NMR (365 MHz, DMSO-d$_6$) δ** = –77.78; **^{31}P**

NMR (162 MHz, DMSO-d$_6$) δ = 46.06; **HRMS (ESI)** calcd for $C_{45}H_{36}AuNOP^+$ (M - OTf)$^+$ 834.2195, found 834.2203.

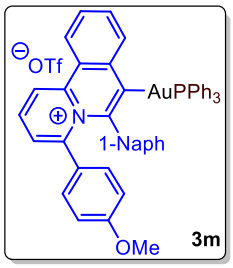


(**3k**): Yellow solid, 101 mg, 90% yield; ***Rf*** **=** 0.40 (CH_2Cl_2/MeOH = 92/08); **^{1}H NMR (500 MHz, DMSO-d$_6$) δ** = 9.42 (d, *J* = 8.2 Hz, 1 H), 9.12 (d, *J* = 8.4 Hz, 1 H), 8.63 (d, *J* = 7.9 Hz, 1 H), 8.53 (t, *J* = 7.9 Hz, 1 H), 8.10 (t, *J* = 7.6 Hz, 1 H), 7.96 (t, *J* = 7.6 Hz, 1 H), 7.85 (d, *J* = 7.2 Hz, 1 H), 7.65 - 7.57 (m, 3 H), 7.52 (t, *J* = 6.7 Hz, 6 H), 7.28 – 7.39(m, *J* = 7.6 Hz, 6 H), 7.09 (d, *J* = 8.7 Hz, 2 H), 6.80 (d, *J* = 8.7 Hz, 2 H), 6.31 (d, *J* = 1.8 Hz, 2 H), 6.26 - 6.20 (m, 1 H), 3.73 (s, 3 H), 3.40 (s, 6 H); **^{13}C NMR (125 MHz, DMSO-d$_6$) δ** = 160.2, 160.0, 149.8, 146.7, 145.1, 144.2, 140.2, 137.9, 133.5 (d, $J_{C\text{-}P}$ = 13.6 Hz), 133.5, 132.9, 131.9, 130.1, 129.8, 129.5 (d, $J_{C\text{-}P}$ = 10.9 Hz), 129.3, 129.1, 127.2, 125.5, 124.3, 120.7 (d, $J_{C\text{-}F}$ = 321.5 Hz), 121.2, 114.0, 107.1, 100.0, 55.3, 54.9; **^{19}F NMR (365 MHz, DMSO-d$_6$) δ** = –77.73; **^{31}P NMR (162 MHz, DMSO-d$_6$) δ** = 41.02; **HRMS (ESI)** calcd for $C_{46}H_{38}AuPO_3N^+$ (M - OTf)$^+$ 880.2252, found 880.2256.

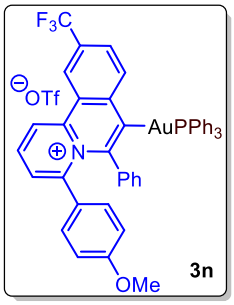


(**3l**): Yellow solid, 83 mg, 75% yield; ***Rf*** **=** 0.30 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (500 MHz, DMSO-d$_6$) δ** = 9.44 (d, *J* = 7.9 Hz, 1 H), 9.13 (d, *J* = 8.4 Hz, 1 H), 8.63 (d, *J* = 7.8 Hz, 1 H), 8.55 (t, *J* = 7.9 Hz, 1 H), 8.11 (t, *J* = 7.5 Hz, 1 H), 7.97 (t, *J* = 7.4 Hz, 1 H), 7.90 (d, *J* = 7.2 Hz, 1 H), 7.65 - 7.57 (m, 3 H), 7.57 - 7.51 (m, 6 H), 7.30 - 7.40 (m, *J* = 8.4 Hz, 6 H), 7.23 (s, 1 H), 7.18 - 7.09 (m, 2 H), 7.08 - 6.97 (m, 3 H), 6.88 (dd, *J* = 2.5, 8.6 Hz, 1 H), 6.75 (dd, *J* = 2.5, 8.6 Hz, 1 H), 3.76 (s, 3 H); **^{13}C NMR (125 MHz, DMSO-d$_6$) δ** = 160.4, 149.4, 146.9, 145.2, 142.7, 140.1, 138.1, 133.7 (d, $J_{C\text{-}P}$ = 13.6 Hz), 133.5, 132.9 (d, $J_{C\text{-}P}$ = 11.8 Hz), 131.9,

129.9, 129.8, 129.7, 129.6 (d, $J_{C\text{-}P}$ = 9.9 Hz), 129.3, 129.0, 127.4, 127.0, 126.9, 125.6, 124.4, 121.4, 120.7 (d, $J_{C\text{-}F}$ = 322.7 Hz), 114.6, 113.8, 55.4; **^{19}F NMR (365 MHz, DMSO-d$_6$) δ** = –77.74; **^{31}P NMR (162 MHz, DMSO-d$_6$) δ** = 41.15; **HRMS (ESI)** calcd for $C_{44}H_{33}AuClNOP^+$ $(M - OTf)^+$ 854.1652, found 854.1659.

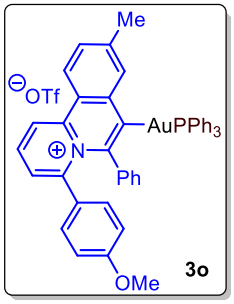


(**3m**): Yellow solid, 88 mg, 86% yield; ***Rf*** **=** 0.30 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (500 MHz, DMSO-d$_6$) δ** = 9.52 (d, *J* = 8.5 Hz, 1 H), 9.20 (d, *J* = 8.4 Hz, 1 H), 8.66 (d, *J* = 7.9 Hz, 1 H), 8.57 - 8.46 (m, 1 H), 8.14 (t, *J* = 7.5 Hz, 1 H), 8.01 (t, *J* = 7.7 Hz, 1 H), 7.73 (t, *J* = 7.5 Hz, 3 H), 7.57 - 7.52 (m, 4 H), 7.44 (t, *J* = 7.0 Hz, 6 H), 7.32 - 7.25 (m, 2 H), 7.23 - 7.19 (m, 1 H), 7.15 (t, *J* = 7.6 Hz, 1 H), 7.04 (br. s., 6 H), 6.85 - 6.79 (m, 1 H), 6.64 (d, *J* = 8.5 Hz, 1 H), 6.53 - 6.45 (m, 1 H), 6.18 (d, *J* = 8.5 Hz, 1 H), 3.49 (s, 3 H); **^{13}C NMR (125 MHz, DMSO-d$_6$) δ** = 159.1, 149.5, 146.6, 142.3, 140.1, 139.5, 137.4, 133.4, (d, $J_{C\text{-}P}$ = 9.08 Hz), 133.4 (d, $J_{C\text{-}P}$ = 12.7 Hz), 133.2, 132.9, 131.7, 130.0, 129.6, 129.2 (d, $J_{C\text{-}P}$ = 9.9 Hz), 129.2 (d, $J_{C\text{-}P}$ = 9.9 Hz), 128.8, 128.7, 128.6, 128.3, 128.0, 127.8, 126.0, 125.8, 125.6, 125.2, 125.1, 124.2, 121.9, 120.7 (d, $J_{C\text{-}F}$ = 321.5 Hz), 114.3, 112.8, 55.1; **^{19}F NMR (365 MHz, DMSO-d$_6$) δ** = –77.71; **^{31}P NMR (162 MHz, DMSO-d$_6$) δ** = 40.78; **HRMS (ESI)** calcd for $C_{48}H_{36}AuPON^+$ $(M - OTf)^+$ 870.2215, found 870.2255.

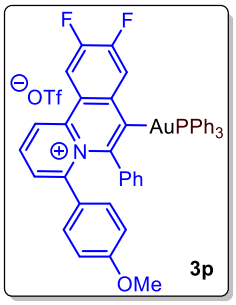


(**3n**): Yellow solid, 86 mg, 83% yield; ***Rf*** **=** 0.30 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (500 MHz, DMSO-d$_6$) δ** = 9.67 (d, *J* = 8.4 Hz, 1 H), 9.49 (s, 1 H), 8.81 (d, *J* = 8.2 Hz, 1 H), 8.61 (t, *J* = 7.9 Hz, 1 H), 8.37 (d, *J* = 8.2 Hz, 1 H), 7.95 (d, *J* = 7.3 Hz, 1 H), 7.63 - 7.58 (m, 3 H), 7.54 (t, *J* = 6.7 Hz, 6 H), 7.38 - 7.30 (m, 6 H), 7.16 (d, *J* = 7.5 Hz, 2 H), 7.11 - 7.06 (m, 3 H),

6.99 - 6.93 (m, 2 H), 6.77 (d, *J* = 8.7 Hz, 2 H), 3.74 (s, 3 H); **^{13}C NMR (125 MHz, DMSO-d$_6$) δ** = 160.3, 150.3, 146.8, 146.2, 143.2, 142.4, 138.7, 134.9, 133.7 (d, $J_{C\text{-}P}$ = 13.6 Hz), 131.9, 130.1, 129.5 (d, $J_{C\text{-}P}$ = 10.9 Hz), 129.3 (d, $J_{C\text{-}P}$ = 3.6 Hz), 129.2, 128.9, 128.5, 128.2, 128.0, 127.5, 125.1, 124.5, 123.5 (q, $J_{C\text{-}F}$ = 4.5 Hz), 122.9, 121.7, 120.7 (d, $J_{C\text{-}F}$ = 322.4 Hz), 114.2, 55.4; **^{19}F NMR (365 MHz, DMSO-d$_6$) δ** = –60.41, –77.75; **^{31}P NMR (162 MHz, DMSO-d$_6$) δ** = 40.99; **HRMS (ESI)** calcd for $C_{45}H_{33}F_3OPN^+$ (M - OTf)$^+$ 888.1895, found 888.1912.

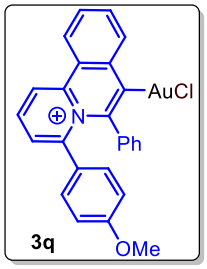


(**3o**): Yellow solid, 92 mg, 85% yields; ***Rf* =** 0.30 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (500 MHz, DMSO-d$_6$) δ** = 9.35 (d, *J* = 8.1 Hz, 1 H), 9.00 (d, *J* = 8.7 Hz, 1 H), 8.48 (t, *J* = 7.6 Hz, 1 H), 8.42 (s, 1 H), 7.79 (d, *J* = 7.6 Hz, 2 H), 7.62 - 7.58 (m, 3 H), 7.56 - 7.52 (m, 6 H), 7.41 - 7.33 (m, 6 H), 7.13 (d, *J* = 7.2 Hz, 2 H), 7.07 - 7.02 (m, 3 H), 6.98 - 6.92 (m, 2 H), 6.75 (d, *J* = 8.9 Hz, 2 H), 3.72 (s, 3 H), 2.59 (s, 3 H); **^{13}C NMR (125 MHz, DMSO-d$_6$) δ** = 160.0, 149.4, 146.7, 144.5, 143.5, 143.4, 140.5, 137.7 (d, $J_{C\text{-}P}$ = 12.7 Hz), 133.6, 133.0, 131.8, 130.9, 130.3, 129.4 (d, $J_{C\text{-}P}$ = 9.9 Hz), 129.3, 128.5, 127.9, 127.1, 126.9, 125.5, 122.0, 120.9, 120.7 (d, $J_{C\text{-}F}$ = 326.0 Hz), 114.1, 55.4, 21.7; **^{19}F NMR (365 MHz, DMSO-d$_6$) δ** = –77.74; **^{31}P NMR (162 MHz, DMSO-d$_6$) δ** = 41.25; **HRMS (ESI)** calcd for $C_{45}H_{36}AuOPN^+$ (M - OTf)$^+$ 834.2213, found 834.2215.

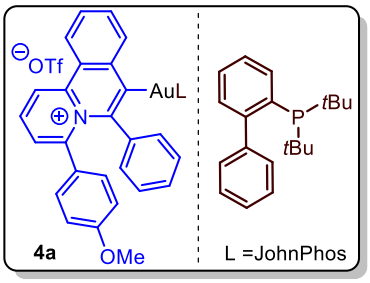


(**3p**):Yellow solid, 87 mg, 79% yield; ***Rf* =** 0.30 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (500 MHz, DMSO-d$_6$) δ** = 9.35 (dd, *J* = 1.1, 8.7 Hz, 1 H), 9.29 (dd, *J* = 7.8, 12.1 Hz, 1 H), 8.56

(dd, *J* = 7.5, 8.4 Hz, 1 H), 8.51 (dd, *J* = 8.2, 11.0 Hz, 1 H), 7.89 (dd, *J* = 1.2, 7.3 Hz, 1 H), 7.65 - 7.56 (m, 3 H), 7.56 - 7.46 (m, 6 H), 7.38 - 7.26 (m, 6 H), 7.14 - 7.09 (m, 2 H), 7.09 - 7.02 (m, 3 H), 6.98 - 6.89 (m, 2 H), 6.79 - 6.69 (m, 2 H), 3.73 (s, 3 H); **^{13}C NMR (125 MHz, DMSO-d$_6$) δ** = 170.6 (d, $J_{C\text{-}P}$ = 109.0 Hz) , 160.3, 151.4, 151.2, 151.1, 150.0, 149.3 (d, $J_{C\text{-}F}$ = 14.5 Hz), 145.9 (d, $J_{C\text{-}F}$ = .3.6 Hz), 145.0, 143.2, 138.9 (d, $J_{C\text{-}F}$ = 7.3 Hz), 138.3, 133.7 (d, $J_{C\text{-}P}$ = 13.6 Hz), 131.9, 130.2, 129.5 (d, $J_{C\text{-}P}$ = 10.9 Hz), 129.5 (d, $J_{C\text{-}P}$ = 6.4 Hz), 129.0, 128.7, 128.1, 127.8, 127.5, 121.9, 121.7, 120.7, 120.4, 120.2, 114.2, 55.5; **^{19}F NMR (365 MHz, DMSO-d$_6$) δ** = –77.75, –128.66, –133.86; **^{31}P NMR (162 MHz, DMSO-d$_6$) δ** = 40.84; **HRMS (ESI)** calcd for $C_{44}H_{32}AuF_2NOP^+$ $(M - OTf)^+$ 856.1790, found 856.1802.

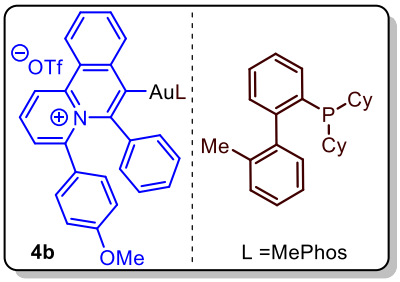


(3q): Yellow solid, 42.4 mg, 52% yield; **^{1}H NMR** (**500 MHz ,DMSO-d$_6$**) **δ** = 9.34 - 9.28 (m, 1 H), 9.00 (d, *J* = 8.4 Hz, 1 H), 8.70 (d, *J* = 8.1 Hz, 1 H), 8.44 (dd, *J* = 7.5, 8.4 Hz, 1 H), 8.04 (t, *J* = 7.6 Hz, 1 H), 7.94 - 7.85 (m, 1 H), 7.72 (dd, *J* = 1.1, 7.2 Hz, 1 H), 7.16 - 7.07 (m, 2 H), 7.07 - 6.98 (m, 5 H), 6.75 (d, *J* = 8.9 Hz, 2 H), 3.75 (s, 3 H); **^{13}C NMR** (**125 MHz, DMSO-d$_6$**) δ = 159.9, 158.1, 149.2, 145.8, 144.2, 142.4, 141.1, 136.9, 135.8, 132.1, 130.6, 129.0, 128.8, 128.7, 127.5, 126.7, 125.0, 123.6, 120.8, 114.0, 55.4; **^{19}F NMR (365 MHz, DMSO-d$_6$) δ** = –77.74; **HRMS (ESI)** calcd for $C_{26}H_{20}AuNO_2$, $(M - Cl + H_2O)^+$ 576.1232, found 576.1242. {Note: The reported HRMS corresponds to the product formed after replacement of chloride by hydroxy from water present in the solvent system that was used for HRMS}

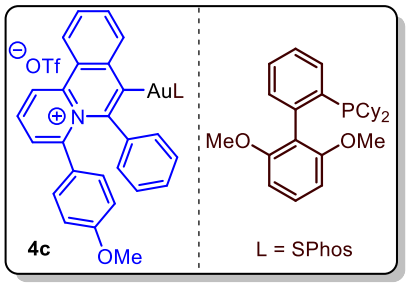


(**4a**): Yellow solid, 80 mg, 72% yield; ***Rf* =** 0.40 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (500 MHz, DMSO-d$_6$) δ** = 9.35 (dd, *J* = 1.1, 8.7 Hz, 1 H), 9.05 (d, *J* = 8.2 Hz, 1 H), 8.47 (dd, *J* =

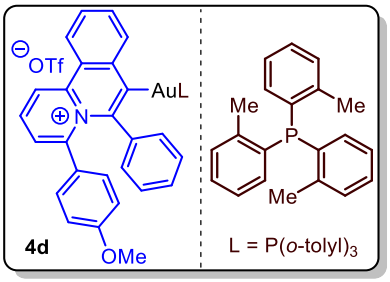
7.5, 8.5 Hz, 1 H), 8.24 (d, *J* = 7.5 Hz, 1 H), 8.02 (t, *J* = 7.6 Hz, 1 H), 7.94 (dd, *J* = 3.1, 6.3 Hz, 1 H), 7.92 - 7.87 (m, 1 H), 7.77 (dd, *J* = 1.1, 7.2 Hz, 1 H), 7.64 - 7.58 (m, 2 H), 7.29 - 7.21 (m, 3 H), 7.14 (br. s., 2 H), 7.00 - 6.89 (m, 6 H), 6.89 - 6.80 (m, 4 H), 3.79 (s, 3 H), 1.14 (br. s., 9 H), 1.11 (br. s., 9 H); **^{13}C NMR (125 MHz, DMSO-d$_6$) δ** = 172.5 (d, $J_{C\text{-}P}$ = 102.6 Hz), 160.1, 149.4, 149.0 (d, $J_{C\text{-}P}$ = 15.4 Hz), 146.3, 143.6, 143.0 (d, $J_{C\text{-}P}$ = 6.3 Hz), 142.8 (d, $J_{C\text{-}P}$ = 3.6 Hz), 140.9, 137.4, 134.8, 134.3, 132.6 (d, $J_{C\text{-}P}$ = 7.2 Hz) 131.8, 130.6, 130.4, 129.1, 129.0, 128.7, 128.5, 128.0, 127.4, 127.0, 126.9, 126.7, 126.6, 126.5, 125.1, 123.8 (d, $J_{C\text{-}P}$ = 3.6 Hz), 120.8, 114.1, 55.5, 36.8 (d, $J_{C\text{-}P}$ = 20.9 Hz), 30.1 (d, $J_{C\text{-}P}$ = 6.3 Hz); **^{19}F NMR (375 MHz, DMSO-d$_6$) δ** = –77.74; **^{31}P NMR (162 MHz, DMSO-d$_6$) δ** = 65.25; **HRMS (ESI)** calcd for $C_{46}H_{46}AuPON^+$ $(M - OTf)^+$ 856.3054, found 856.3075.



(**4b**): Yellow solid, 88 mg, 75% yield; ***Rf* =** 0.40 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (500 MHz, DMSO-d$_6$) δ** = 9.43 - 9.30 (m, 1 H), 9.07 (d, *J* = 8.4 Hz, 1 H), 8.55 - 8.46 (m, 1 H), 8.25 (d, *J* = 7.8 Hz, 1 H), 8.03 (t, *J* = 7.3 Hz, 1 H), 7.91 (t, *J* = 7.6 Hz, 1 H), 7.84 - 7.74 (m, 2 H), 7.62 - 7.52 (m, 2 H), 7.19 - 7.12 (m, 1 H), 7.06 - 6.94 (m, 6 H), 6.94 - 6.89 (m, 2 H), 6.89 - 6.82 (m, 2 H), 6.80 (d, *J* = 7.3 Hz, 2 H), 6.76 - 6.70 (m, 1 H), 3.78 (s, 3 H), 2.22 - 2.07 (m, 1 H), 1.87 (s, 3 H), 1.73 (br. s., 3 H), 1.64 (br. s., 3 H), 1.57 (br. s., 3 H), 1.33 (s, 1 H), 1.26 - 1.11 (m, 7 H), 1.04 - 0.92 (m, 4 H); **^{13}C NMR (125 MHz, DMSO-d$_6$) δ** = 173.5 (d, $J_{C\text{-}P}$ = 105.3 Hz), 160.1, 149.5, 147.8 (d, $J_{C\text{-}P}$ = 14.5 Hz), 146.3, 143.4, 143.2 (d, $J_{C\text{-}P}$ = 4.5 Hz), 141.6 (d, $J_{C\text{-}P}$ = 5.4 Hz), 141.0, 137.5, 134.8, 134.0, 133.5, 131.7, 130.9, 130.4 (d, $J_{C\text{-}P}$ = 9.08 Hz), 129.6, 129.0, 128.8, 128.2, 127.8, 127.7, 127.2, 127.0, 126.7, 126.5, 126.1, 125.6, 125.2, 123.9 (d, $J_{C\text{-}P}$ = 3.6 Hz), 120.7 (d, $J_{C\text{-}F}$ = 322.4 Hz), 120.8, 114.3, 113.9, 55.5, 36.6 (d, $J_{C\text{-}P}$ = 28.2 Hz), 34.2 (d, $J_{C\text{-}P}$ = 30.9 Hz), 30.4, 28.8, 28.3, 26.0 (d, $J_{C\text{-}P}$ = 10.9 Hz), 25.6 (d, $J_{C\text{-}P}$ = 3.6 Hz), 25.5, 25.3 (d, $J_{C\text{-}P}$ = 16.3 Hz), 20.6; **^{19}F NMR (375 MHz, DMSO-d$_6$) δ** = –77.74; **^{31}P NMR (162 MHz, DMSO-d$_6$) δ** = 44.25; **HRMS (ESI)** calcd for $C_{51}H_{52}AuOPN^+$ $(M - OTf)^+$ 922.3445, found 922.3449.

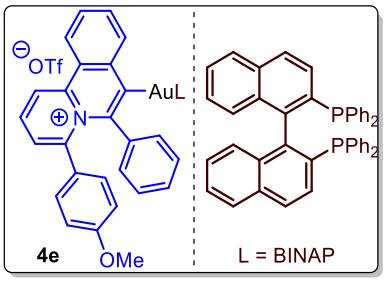


(**4c**): Yellow solid, 101 mg, 82% yield; ***Rf*** **=** 0.40 (CH_2Cl_2/MeOH = 90/10); **^{1}H NMR (500 MHz, DMSO-d$_6$) δ** = 9.37 (dd, *J* = 1.1, 8.8 Hz, 1 H), 9.07 (d, *J* = 8.4 Hz, 1 H), 8.49 (dd, *J* = 7.5, 8.5 Hz, 1 H), 8.36 (d, *J* = 7.3 Hz, 1 H), 8.08 - 7.98 (m, 1 H), 7.96 - 7.87 (m, 1 H), 7.79 (dd, *J* = 1.1, 7.4 Hz, 1 H), 7.76 - 7.68 (m, 1 H), 7.49 (t, *J* = 6.9 Hz, 2 H), 7.05 - 6.95 (m, 6 H), 6.95 - 6.91 (m, 2 H), 6.90 - 6.82 (m, 3 H), 6.36 (d, *J* = 8.4 Hz, 2 H), 3.77 (s, 3 H), 3.58 (s, 6 H), 2.36 - 2.25 (m, 2 H), 1.76 (d, *J* = 11.4 Hz, 2 H), 1.66 (d, *J* = 11.7 Hz, 2 H), 1.58 (t, *J* = 12.5 Hz, 4 H), 1.53 - 1.44 (m, 2 H), 1.17 (quin, *J* = 13.2 Hz, 4 H), 1.09 - 0.95 (m, 6 H); **^{13}C NMR (125 MHz, DMSO-d$_6$) δ** = 173.6 (d, $J_{C\text{-}P}$ = 105.3 Hz), 160.0, 156.8, 149.5, 146.3, 143.5, 143.3 (d, $J_{C\text{-}P}$ = 4.6 Hz), 141.8 (d, $J_{C\text{-}P}$ = 14.8 Hz), 141.1, 137.5, 134.0, 132.8, 132.5 (d, $J_{C\text{-}P}$ = 8.1 Hz), 131.7, 130.7, 130.4, 129.2, 129.2, 129.1, 128.9, 128.5, 127.8, 127.4, 127.0, 126.8, 125.2, 123.9 (d, $J_{C\text{-}P}$ = 4.5 Hz), 120.9, 120.7, 118.8, 118.8, 114.0, 103.9, 55.5, 55.0, 35.8 (d, $J_{C\text{-}P}$ = 30.0 Hz), 30.1 (d, $J_{C\text{-}P}$ = 5.4 Hz), 28.8, 26.1 (d, $J_{C\text{-}P}$ = 11.81 Hz) 26.0 (d, $J_{C\text{-}P}$ = 13.6 Hz), 25.5; **^{19}F NMR (375 MHz, DMSO-d$_6$) δ** = –77.74; **^{31}P NMR (162 MHz, DMSO-d$_6$) δ** = 46.05; **HRMS (ESI)** calcd for $C_{52}H_{54}AuO_3PN^+$ $(M - OTf)^+$ 968.3512, found 968.3517.

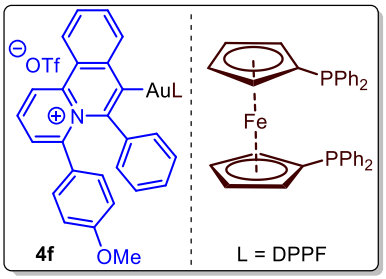


(**4d**): Yellow solid, 93 mg, 84% yield; ***Rf*** **=** 0.30 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (500 MHz, DMSO-d$_6$) δ** = 9.44 - 9.32 (m, 1 H), 9.08 (d, *J* = 8.4 Hz, 1 H), 8.51 (dd, *J* = 7.6, 8.3 Hz, 1 H), 8.44 (d, *J* = 7.6 Hz, 1 H), 8.05 (t, *J* = 7.6 Hz, 1 H), 7.98 - 7.90 (m, 1 H), 7.82 (dd, *J* = 1.1, 7.3 Hz, 1 H), 7.59 - 7.49 (m, 3 H), 7.46 - 7.40 (m, 3 H), 7.30 (t, *J* = 7.6 Hz, 3 H), 7.05 - 6.98 (m, *J* = 8.9 Hz, 2 H), 6.95 (d, *J* = 7.3 Hz, 2 H), 6.86 (t, *J* = 7.4 Hz, 1 H), 6.79 (m, 3 H),

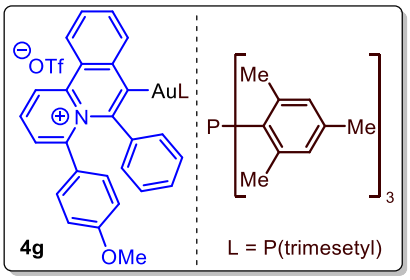
6.75 - 6.69 (m, *J* = 8.7 Hz, 2 H), 6.61 (t, *J* = 7.8 Hz, 2 H), 3.72 (s, 3 H), 2.34 (s, 9 H);**^{13}C NMR (125 MHz, DMSO-d$_6$) δ** = 169.7 (d, J_{C-P} = 109.0 Hz), 160.1, 149.7, 146.8, 144.3, 144.3 (d, J_{C-P} = 4.5 Hz), 142.0 (d, J_{C-P} = 13.6 Hz), 140.1, 137.9, 133.3, 132.9 (d, J_{C-P} = 9.1 Hz) 132.6, 132.2 (d, J_{C-P} = 8.2 Hz) 131.9, 130.3, 129.3, 128.3, 127.7, 127.3, 127.1 (d, J_{C-P} = 4.5 Hz), 127.0, 125.7, 125.6, 125.3, 124.1, 124.1 (d, J_{C-P} = 4.5 Hz) 120.7 (d, J_{C-F} = 322.4 Hz), 114.0, 55.4, 22.2 (d, J_{C-P} = 10.0 Hz); **^{19}F NMR (375 MHz, DMSO-d$_6$) δ** = –77.73; **^{31}P NMR (162 MHz, DMSO-d$_6$) δ** = 25.25; **HRMS (ESI)** calcd for $C_{47}H_{40}AuPON^+$ (M - OTf)$^+$ 862.2556, found 862.2571.



(**4e**): Yellow solid, 190.5 mg, 85% yield; ***Rf* =** 0.50 (CH_2Cl_2/MeOH = 90/10); **^{1}H NMR (500 MHz, DMSO-d$_6$) δ** = 9.35 (dd, *J* = 1.1, 8.9 Hz, 2 H), 9.03 (d, *J* = 8.5 Hz, 2 H), 8.49 (dd, *J* = 7.6, 8.3 Hz, 2 H), 7.97 (d, *J* = 8.7 Hz, 2 H), 7.90 - 7.83 (m, 4 H), 7.78 - 7.71 (m, 4 H), 7.61 - 7.54 (m, 4 H), 7.41 - 7.32 (m, 10 H), 7.23 (dt, *J* = 2.3, 7.8 Hz, 4 H), 7.17 (m, 4 H), 7.06 (t, *J* = 7.9 Hz, 2 H), 6.98 (d, *J* = 9.2 Hz, 2 H), 6.84 (d, *J* = 7.8 Hz, 2 H), 6.80 - 6.72 (m, 8 H), 6.72 - 6.65 (m, 6 H), 6.56 - 6.50 (m, *J* = 7.6 Hz, 2 H), 6.47 - 6.38 (m, *J* = 7.5 Hz, 2 H), 6.17 (t, *J* = 7.3 Hz, 2 H), 3.76 (s, 6 H); **^{13}C NMR (125 MHz, DMSO-d$_6$) δ** = 169.3, (d, J_{C-P} = 109.9 Hz), 160.0, 149.7, 146.5, 143.5 (d, J_{C-P} = 143.5 Hz), 142.7, 139.7, 137.9, 134.2 (d, J_{C-P} = 8.2 Hz), 134.0 (d, J_{C-P} = 16.3 Hz), 133.4 (d, J_{C-P} = 10.0 Hz), 132.8 (d, J_{C-P} = 13.6 Hz), 132.0, 131.6, 131.4, 130.9 (d, J_{C-P} = 7.3 Hz), 130.4, 130.3, 130.1, 129.6, 129.4 (d, J_{C-P} = 10.9 Hz), 129.0 (d, J_{C-P} = 9.1 Hz), 128.4, 128.2, 127.8, 127.6, 127.4, 127.2, 126.8, 126.4, 125.3, 123.9, (d, J_{C-P} = 3.7 Hz), 120.9, 120.7 (d, J_{C-F} = 322.4 Hz), 114.0 (d, J_{C-P} = 46.3 Hz), 55.5; **^{19}F NMR (375 MHz, DMSO-d$_6$) δ** = –72.72; **^{31}P NMR (162 MHz, DMSO-d$_6$) δ** = 34.17; **HRMS (ESI)** calcd for $[C_{96}H_{70}Au_2N_2O_2P_2]^{2+}$ (M - OTf)$^{2+}$ 869.2116, found 869.2134.

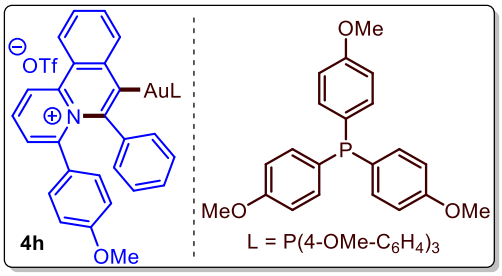


(**4f**): Yellow solid, 156 mg, 72% yield; ***Rf*** **=** 0.50 (CH_2Cl_2/MeOH = 90/10); **^{1}H NMR (500 MHz, DMSO-d$_6$) δ** = 9.44 (d, *J* = 8.5 Hz, 2 H), 9.14 (d, *J* = 8.4 Hz, 2 H), 8.74 - 8.60 (m, *J* = 7.9 Hz, 2 H), 8.55 (t, *J* = 7.9 Hz, 2 H), 8.06 (t, *J* = 7.5 Hz, 2 H), 7.95 (t, *J* = 7.6 Hz, 2 H), 7.90 - 7.81 (m, *J* = 7.3 Hz, 2 H), 7.46 (d, *J* = 6.7 Hz, 4 H), 7.45 - 7.37 (m, 8 H), 7.25 (m, 8 H), 7.14 (d, *J* = 7.3 Hz, 4 H), 7.09 - 6.94 (m, 10 H), 6.76 (d, *J* = 8.7 Hz, 4 H), 4.29 (br. s., 4 H), 3.94 (br. s., 4 H), 3.73 (s, 6 H); **^{13}C NMR (125 MHz, DMSO-d$_6$) δ** = 171.4 (d, $J_{C\text{-}P}$ = 117.1 Hz), 160.0, 149.7, 146.7, 144.3 (d, $J_{C\text{-}P}$ = 4.5 Hz), 143.5, 140.4, 138.1, 132.8 (d, $J_{C\text{-}P}$ = 14.5 Hz), 131.5, 130.8, 130.4, (d, $J_{C\text{-}P}$ = 17.2 Hz), 129.1 (d, $J_{C\text{-}P}$ = 9 Hz), 129.0, 128.6, 128.1, 127.2, 124.1, 120.7 (d, $J_{C\text{-}F}$ = 321.5 Hz), 114.0, 74.2 (d, $J_{C\text{-}P}$ = 12.7 Hz), 70.9 (d, $J_{C\text{-}P}$ = 62.6 Hz), 55.4; **^{19}F NMR (375 MHz, DMSO-d$_6$) δ** = –77.73; **^{31}P NMR (162 MHz, DMSO-d$_6$) δ** = 35.51; **HRMS (ESI)** calcd for $[C_{86}H_{66}Au_2FeN_2O_2P_2]^{2+}$ $(M - OTf)^+$ 835.1636 found 835.1660.

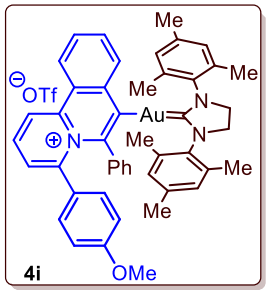


(**4g**): Yellow solid, 105 mg, 87% yield; ***Rf*** **=** 0.30 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (400 MHz, DMSO-d$_6$) δ** = 9.34 (d, *J* = 8.3 Hz, 1 H), 9.04 (d, *J* = 8.3 Hz, 1 H), 8.48 (t, *J* = 7.9 Hz, 1 H), 8.23 (d, *J* = 7.8 Hz, 1 H), 8.01 (t, *J* = 7.5 Hz, 1 H), 7.90 (t, *J* = 7.6 Hz, 1 H), 7.78 (d, *J* = 7.2 Hz, 1 H), 6.99 - 6.87 (m, 9 H), 6.79 (d, *J* = 7.6 Hz, 2 H), 6.73 (d, *J* = 8.6 Hz, 2 H), 6.56 (t, *J* = 7.5 Hz, 2 H), 3.75 (s, 3 H), 2.28 (s, 9 H), 2.08 (s, 18 H); **^{13}C NMR (100 MHz, DMSO-d$_6$) δ** = 166.5 (d, $J_{C\text{-}P}$ = 107.1 Hz), 160.0, 149.7, 146.7, 143.8 (d, $J_{C\text{-}P}$ = 4.4 Hz), 143.3 (d, $J_{C\text{-}P}$ = 1.5 Hz), 142.4, 142.3, 140.5 (d, $J_{C\text{-}P}$ = 2.2 Hz), 140.2, 137.8, 133.6, 132.3, 131.2 (d, $J_{C\text{-}P}$ = 8.8 Hz), 130.4, 129.1, 128.4, 127.7, 127.4 (d, $J_{C\text{-}P}$ = 11.7 Hz), 125.8, 125.4, 123.9 (d, $J_{C\text{-}P}$ = 4.4 Hz), 120.9, 114.0, 55.4, 23.6 (d, $J_{C\text{-}P}$ = 9.5 Hz) 20.4; **^{19}F NMR (375 MHz, DMSO-d$_6$) δ** =

–77.74; **^{31}P NMR (162 MHz, DMSO-d$_6$) δ** = 11.90; **HRMS (ESI)** calcd for $C_{53}H_{52}AuPON^+$ $(M - OTf)^+$ 946.3247, found 946.3219.

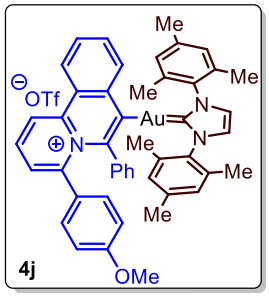


(**4h**): Yellow solid, 91 mg, 78% yield; ***Rf*** **=** 0.30 (CH_2Cl_2/MeOH = 90/10); **^{1}H NMR (500 MHz, DMSO-d$_6$) δ** = 9.41 (d, *J* = 8.4 Hz, 1 H), 9.11 (d, *J* = 8.4 Hz, 1 H), 8.63 (d, *J* = 7.9 Hz, 1 H), 8.52 (t, *J* = 7.9 Hz, 1 H), 8.10 (t, *J* = 7.5 Hz, 1 H), 7.95 (t, *J* = 7.6 Hz, 1 H), 7.84 (d, *J* = 7.2 Hz, 1 H), 7.23 (m, *J* = 8.7 Hz, 6 H), 7.13 (d, *J* = 7.3 Hz, 2 H), 7.11 - 7.03 (m, 9 H), 7.01 - 6.95 (m, 2 H), 6.76 (d, *J* = 8.7 Hz, 2 H), 3.80 (s, 9 H), 3.74 (s, 3 H); **^{13}C NMR (100 MHz, DMSO-d$_6$) δ** = 162.2, 160.6, 150.2, 147.3, 143.9, 141.0, 138.3, 135.6 (d, J_{C-P} = 15.4 Hz), 134.0, 133.3, 130.8, 129.8, 129.1, 128.6, 127.7 (d, J_{C-P} = 13.9 Hz), 126.0, 121.6, 121.1, 115.5 (d, J_{C-P} = 12.5 Hz), 114.6, 55.9, 55.9; **^{19}F NMR (375 MHz, DMSO-d$_6$) δ** = –72.99; **^{31}P NMR (162 MHz, DMSO-d$_6$) δ** = 42.28; **HRMS (ESI)** calcd for $C_{48}H_{40}AuPO_4N^+$ $(M - OTf)^+$ 910.1887, found 910.1878.



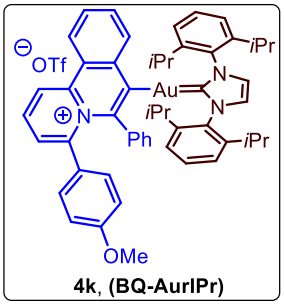
(4i): Yellow solid, 96 mg, 86% yield; ***Rf*** **=** 0.30 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (500 MHz, DMSO-d$_6$) δ** = 9.22 (d, *J* = 7.9 Hz, 1 H), 8.90 (d, *J* = 8.4 Hz, 1 H), 8.41 - 8.33 (m, 1 H), 7.79 (t, *J* = 7.3 Hz, 1 H), 7.69 (t, *J* = 7.5 Hz, 1 H), 7.65 (d, *J* = 7.3 Hz, 1 H), 7.61 (d, *J* = 7.9 Hz, 1 H), 7.02 (s, 4 H), 6.93 - 6.87 (m, 1 H), 6.86 - 6.81 (m, *J* = 8.7 Hz, 2 H), 6.69 (t, *J* = 7.8 Hz, 2 H), 6.67 - 6.63 (m, *J* = 8.7 Hz, 2 H), 6.51 (d, *J* = 7.3 Hz, 2 H), 4.01 (s, 4 H), 3.74 (s, 3 H), 2.30 (s, 6 H), 2.23 (s, 12 H);**^{13}C NMR (100 MHz, DMSO-d$_6$) δ** = 209.0, 168.3, 159.8, 149.2, 146.3, 144.2, 143.0, 141.6, 137.7, 137.1, 135.5, 135.1, 133.5, 131.4, 130.3, 129.2, 128.8, 128.6, 127.6, 127.4, 126.7, 126.5, 125.0, 123.6, 120.7, 119.1, 113.8, 55.4, 50.7, 20.6,

17.4;**^{19}F NMR (375 MHz, DMSO-d$_6$) δ** = –77.74; **HRMS (ESI)** calcd for $C_{47}H_{45}AuON_3^+$ (M - OTf)$^+$864.3445, found 864.3465.



4j

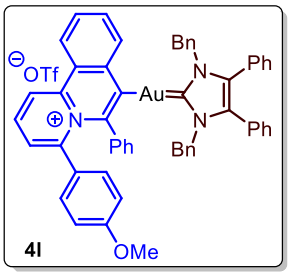
(4j): Yellow solid, 100 mg, 90% yield; ***Rf*= 0.30** (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (700 MHz, DMSO-d$_6$) δ** = 9.25 - 9.22 (m, 1 H), 8.92 (d, *J* = 8.4 Hz, 1 H), 8.38 (dd, *J* = 7.4, 8.4 Hz, 1 H), 7.82 - 7.79 (m, 1 H), 7.74 - 7.72 (m, 2 H), 7.71 (d, *J* = 7.3 Hz, 1 H), 7.70 - 7.68 (m, 1 H), 7.66 (dd, *J* = 1.1, 7.2 Hz, 1 H), 7.12 (s, 4 H), 6.90 (t, *J* = 7.4 Hz, 1 H), 6.87 - 6.84 (m, 2 H), 6.71 - 6.63 (m, 4 H), 6.58 (d, *J* = 7.3 Hz, 2 H), 3.74 (s, 3 H), 2.37 (s, 6 H), 2.00 (s, 12 H); **^{13}C NMR (125 MHz, DMSO-d$_6$) δ** = 188.1, 168.5, 159.9, 149.2, 146.2, 144.1, 143.2, 141.7, 138.7, 137.2, 135.0, 134.4, 133.6, 131.5, 130.4, 129.0, 128.8, 128.7, 127.7, 127.4, 126.8, 126.5, 125.0, 123.6, 123.5, 120.7, 113.9, 55.4, 20.7, 17.2;**^{19}F NMR (375 MHz, DMSO-d$_6$) δ** = –77.74; **HRMS (ESI)** calcd for $C_{47}H_{43}AuON_3^+$ (M - OTf)$^+$862.2741, found 862.2758.



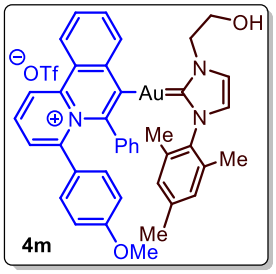
4k, (BQ-AurIPr)

(**4k**): Yellow solid, 106 mg, 88% yield; ***Rf* =** 0.40 (CH_2Cl_2/MeOH = 92/08); **^{1}H NMR (500 MHz, DMSO-d$_6$) δ** = 9.20 (dd, *J* = 1.2, 8.9 Hz, 1 H), 8.89 (d, *J* = 8.4 Hz, 1 H), 8.34 (dd, *J* = 7.3, 8.5 Hz, 1 H), 7.92 (s, 2 H), 7.79 - 7.69 (m, 3 H), 7.62 (dd, *J* = 1.2, 7.2 Hz, 1 H), 7.56 - 7.49 (m, 1 H), 7.46 (d, *J* = 7.9 Hz, 4 H), 7.13 (d, *J* = 7.3 Hz, 1 H), 6.85 - 6.77 (m, 2 H), 6.74 (t, *J* = 7.4 Hz, 1 H), 6.65 - 6.59 (m, *J* = 8.9 Hz, 2 H), 6.55 (d, *J* = 7.2 Hz, 2 H), 6.37 (t, *J* = 7.8 Hz, 2 H), 3.73 (s, 3 H), 2.49 - 2.45 (m, 4 H), 1.17 (d, *J* = 7.0 Hz, 12 H), 1.05 (d, *J* = 6.7 Hz, 12 H);**^{13}C NMR (125 MHz, DMSO-d$_6$) δ** = 189.7, 168.2, 159.7, 149.1, 146.2, 145.2, 144.3, 142.9, 141.7, 137.0, 134.4, 133.7, 131.7, 130.5, 130.4, 128.7, 128.5, 127.4, 127.4, 126.7,

126.3, 124.9, 124.8, 124.1, 123.4, 120.8, 120.7 (d, $J_{C\text{-}F}$ = 322.4 Hz), 116.9, 113.7, 55.4, 28.3, 23.9, 23.4; **^{19}F NMR (375 MHz, DMSO-d$_6$) δ** = –77.74; **HRMS (ESI)** calcd for $C_{53}H_{55}AuON_3^+$ (M - OTf)$^+$ 946.4187, found 946.4175.

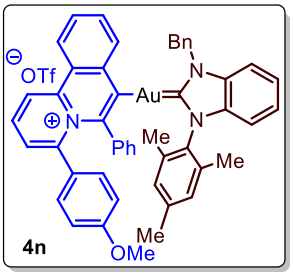


(**4l**): Yellow solid, 79 mg, 65% yield; ***Rf*** **=** 0.30 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (400 MHz, DMSO-d$_6$) δ** = 9.32 (d, *J* = 8.1 Hz, 1 H), 9.01 (d, *J* = 8.3 Hz, 1 H), 8.49 - 8.41 (m, 1 H), 8.24 (d, *J* = 7.9 Hz, 1 H), 7.89 - 7.82 (m, 1 H), 7.81 - 7.73 (m, 2 H), 7.36 - 7.24 (m, 12 H), 7.16 (d, *J* = 7.1 Hz, 4 H), 7.01 - 6.94 (m, 4 H), 6.93 - 6.82 (m, 7 H), 6.71 (d, *J* = 8.8 Hz, 2 H), 5.30 (s, 4 H), 3.73 (s, 3 H); **^{13}C NMR (175 MHz, DMSO-d$_6$) δ** = 187.7, 168.8, 159.9, 149.3, 146.4, 144.2, 143.8, 141.4, 137.3, 136.5, 136.2, 133.9, 132.3, 132.1, 131.9, 130.7, 130.6, 130.5, 129.5, 129.3, 129.0, 128.9, 128.6, 128.5, 127.8, 127.7, 127.6, 127.1, 127.0, 126.8, 126.5, 126.3, 125.2, 123.7, 120.9, 120.6 (d, $J_{C\text{-}F}$ = 321.7 Hz), 114.0, 55.4, 51.4; **^{19}F NMR (375 MHz, DMSO-d$_6$) δ** = –77.74; **HRMS (ESI)** calcd for $C_{55}H_{43}AuON_3^+$ (M - OTf)$^+$ 958.3115, found 958.3126.

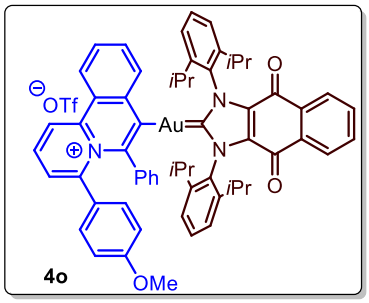


(4m): Yellow solid, 62 mg, 60% yield; ***Rf*** **=** 0.20 (CH_2Cl_2/MeOH = 90/10); **^{1}H NMR (500 MHz, DMSO-d$_6$) δ** = 9.30 (d, *J* = 8.1 Hz, 1 H), 8.97 (d, *J* = 8.5 Hz, 1 H), 8.43 (t, *J* = 7.9 Hz, 1 H), 7.87 - 7.79 (m, 1 H), 7.79 - 7.70 (m, 1 H), 7.70 - 7.62 (m, 2 H), 7.60 (d, *J* = 1.7 Hz, 1 H), 7.45 (d, *J* = 1.5 Hz, 1 H), 7.19 (s, 2 H), 7.11 - 7.02 (m, 3 H), 7.02 - 6.93 (m, 4 H), 6.73 (d, *J* = 8.9 Hz, 2 H), 4.95 (t, *J* = 5.0 Hz, 1 H), 3.95 (t, *J* = 5.3 Hz, 2 H), 3.74 (s, 3 H), 3.56 (q, *J* = 5.1 Hz, 2 H), 2.45 (s, 3 H), 1.95 (s, 6 H); **^{13}C NMR (100 MHz, DMSO-d$_6$) δ** = 187.0, 169.5, 168.9, 159.9, 149.2, 146.2, 144.0, 143.8, 141.6, 138.7, 137.1, 135.6, 134.9, 133.7, 131.5, 130.5, 129.0, 128.8, 128.5, 127.7, 126.9, 126.8, 125.1, 123.6, 122.8, 122.2, 120.9, 120.7 (d,

$J_{C\text{-}F}$ = 322.0 Hz), 114.0, 60.7, 55.4, 52.2, 20.8, 17.4; **^{19}F NMR (375 MHz, DMSO-d$_6$) δ** = –77.74; **HRMS (ESI)** calcd for $C_{40}H_{37}AuO_2N_3^+$ (M - OTf)$^+$, 788.2621, found 788.2605.

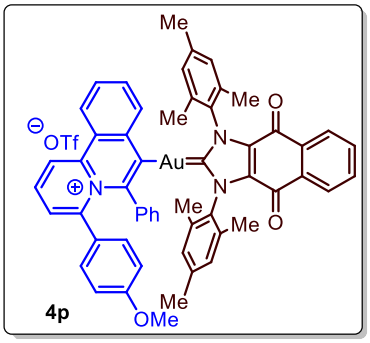


(4n): Yellow solid, 76 mg, 67% yield; ***Rf*** **=** 0.30 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (500 MHz, DMSO-d$_6$) δ** = 9.32 (d, *J* = 7.9 Hz, 1 H), 9.00 (d, *J* = 8.5 Hz, 1 H), 8.49 - 8.40 (m, 1 H), 7.91 - 7.83 (m, 1 H), 7.79 - 7.71 (m, 2 H), 7.68 (t, *J* = 7.6 Hz, 1 H), 7.61 (d, *J* = 7.8 Hz, 1 H), 7.45 (t, *J* = 7.4 Hz, 1 H), 7.40 (t, *J* = 7.5 Hz, 1 H), 7.36 - 7.27 (m, 5 H), 7.25 - 7.17 (m, 2 H), 7.12 (d, *J* = 8.1 Hz, 1 H), 7.00 - 6.93 (m, 4 H), 6.86 (t, *J* = 7.4 Hz, 1 H), 6.79 (t, *J* = 7.5 Hz, 2 H), 6.69 (d, *J* = 8.7 Hz, 2 H), 5.48 (s, 2 H), 3.71 (s, 3 H), 2.53 (s, 3 H), 1.91 (s, 6 H); **^{13}C NMR (100 MHz, DMSO-d$_6$) δ** =195.2, 168.6, 167.9, 159.9, 149.3, 146.4, 144.3, 143.8, 141.4, 140.4, 139.6, 137.4, 135.6, 135.5, 133.5, 132.3, 132.1, 131.6, 130.4, 129.4, 129.1, 128.9, 128.7, 128.5, 128.0, 127.6, 127.0, 126.9, 126.7, 125.4, 125.2, 124.8, 123.8, 120.9, 114.0, 112.8, 111.4, 55.4, 50.7, 20.9, 17.2; **^{19}F NMR (375 MHz, DMSO-d$_6$) δ** = –77.74; **HRMS (ESI)** calcd for $C_{49}H_{41}AuON_3^+$ (M - OTf)$^+$ 884.2933, found 884.2910.

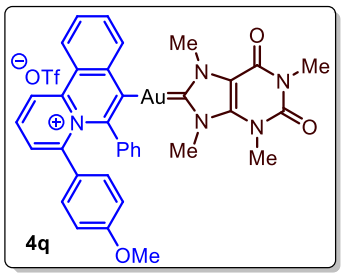


(4o): Yellow solid, 123 mg, 91% yield; ***Rf*** **=** 0.30 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (500 MHz, DMSO-d$_6$) δ** = 9.21 (d, *J* = 8.4 Hz, 1 H), 8.90 (d, *J* = 8.4 Hz, 1 H), 8.35 (t, *J* = 7.9 Hz, 1 H), 8.05 - 7.98 (m, 2 H), 7.93 - 7.87 (m, 2 H), 7.83 - 7.76 (m, 3 H), 7.64 - 7.60 (m, 2 H), 7.49 (d, *J* = 7.8 Hz, 4 H), 7.04 (d, *J* = 7.9 Hz, 1 H), 6.80 (d, *J* = 8.5 Hz, 3 H), 6.64 (d, *J* = 8.7 Hz, 2 H), 6.51 - 6.43 (m, 4 H), 3.77 (s, 3 H), 2.61 (m, *J* = 4 H), 1.06 (t, *J* = 6.3 Hz, 24 H); **^{13}C NMR (100 MHz, DMSO-d$_6$) δ** 198.5, 175.2, 167.1, 160.6, 150.1, 146.9, 145.6, 145.6, 143.4, 142.0, 138.4, 135.9, 134.5, 133.4, 133.1, 132.7, 131.9, 131.1, 129.7, 129.3, 128.7, 127.9,

127.5, 127.4, 127.3, 125.6, 125.3, 123.9, 122.0, 121.2, 121.1, 114.7, 56.2, 29.2, 24.7, 23.8; **^{19}F NMR (375 MHz, DMSO-d$_6$) δ** = –77.74; **HRMS (ESI)** calcd for $C_{61}H_{57}AuO_3N_3^+$ (M - OTf)$^+$ 1076.4030, found 1076.4060.

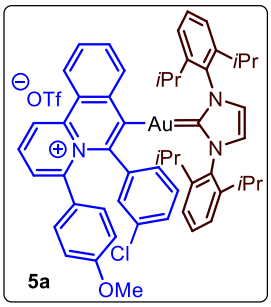


(4p): Yellow solid, 109 mg, 87% yield; ***Rf* =** 0.30 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (400 MHz, DMSO-d$_6$) δ** = 9.25 (d, *J* = 8.2 Hz, 1 H), 8.94 (d, *J* = 7.8 Hz, 1 H), 8.39 (t, *J* = 7.9 Hz, 1 H), 8.06 - 7.94 (m, 2 H), 7.94 - 7.86 (m, 2 H), 7.86 - 7.77 (m, 2 H), 7.69 (m, *J* = 7.3 Hz, 2 H), 7.13 (s, 4 H), 7.00 - 6.94 (m, 1 H), 6.90 - 6.82 (m, *J* = 8.7 Hz, 2 H), 6.79 (t, *J* = 7.6 Hz, 2 H), 6.71 - 6.63 (m, *J* = 8.8 Hz, 2 H), 6.56 (d, *J* = 7.3 Hz, 2 H), 3.75 (s, 3 H), 2.39 (s, 6 H), 2.02 (s, 12 H); **^{13}C NMR (100 MHz, DMSO-d$_6$) δ** 196.2, 174.4, 167.0, 159.9, 149.4, 146.4, 144.4, 143.0, 141.4, 139.0, 137.3, 134.4, 134.2, 133.4, 133.2, 132.4, 132.2, 131.6, 130.3, 129.1, 128.8, 128.7, 127.7, 127.6, 126.8, 126.2, 125.1, 123.7, 120.7, 113.8, 55.4, 20.8, 17.4; **^{19}F NMR (375 MHz, DMSO-d$_6$) δ** = –77.73; **HRMS (ESI)** calcd for $C_{55}H_{45}AuO_3N_3^+$ (M - OTf)$^+$ 992.3116, found 992.3121.

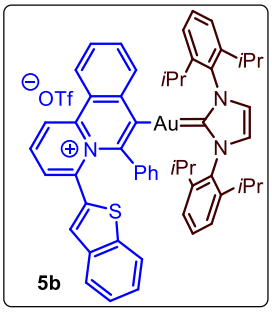


(4q): Yellow solid, 89 mg, 88% yield; ***Rf* =** 0.30 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (500 MHz, DMSO-d$_6$) δ** = 9.40 (d, *J* = 8.2 Hz, 1 H), 9.10 (d, *J* = 8.4 Hz, 1 H), 8.73 (d, *J* = 7.8 Hz, 1 H), 8.51 (t, *J* = 7.6 Hz, 1 H), 8.09 (t, *J* = 7.1 Hz, 1 H), 7.95 (t, *J* = 7.2 Hz, 1 H), 7.83 (d, *J* = 7.0 Hz, 1 H), 7.11 (m, 5 H), 7.07 - 7.03 (m, *J* = 8.2 Hz, 2 H), 6.81 - 6.76 (m, *J* = 8.2 Hz, 2 H), 3.99 (s, 3 H), 3.86 (s, 3 H), 3.76 (s, 3 H), 3.69 (s, 3 H), 3.22 (s, 3 H); **^{13}C NMR (125 MHz, DMSO-d$_6$) δ =** 191.1, 168.4, 160.0, 153.1, 150.4, 149.5, 146.4, 144.3, 143.8, 141.3, 140.3,

137.5, 133.9, 132.5, 130.4, 129.1, 128.8, 127.9, 127.3, 127.2, 126.9, 125.4, 123.8, 121.0, 114.1, 108.2, 55.4, 38.0, 36.5, 31.4, 28.2; **^{19}F NMR (375 MHz, DMSO-d$_6$) δ** = –77.74; **HRMS (ESI)** calcd for $C_{35}H_{31}AuO_3N_5^+$ $(M - OTf)^+$ 766.2108, found 766.2087.

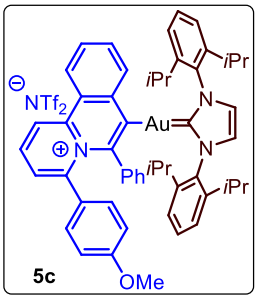


(5a): Yellow solid, 97 mg, 78% yield; ***Rf* =** 0.30 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (500 MHz, DMSO-d$_6$) δ** = 9.22 (d, *J* = 8.1 Hz, 1 H), 8.90 (d, *J* = 8.5 Hz, 1 H), 8.41 - 8.33 (m, 1 H), 7.91 (s, 2 H), 7.81 - 7.72 (m, 3 H), 7.66 (d, *J* = 6.6 Hz, 1 H), 7.53 (t, *J* = 7.6 Hz, 1 H), 7.48 (d, *J* = 7.8 Hz, 2 H), 7.40 (d, *J* = 7.8 Hz, 2 H), 7.10 (d, *J* = 7.9 Hz, 1 H), 6.92 (d, *J* = 8.5 Hz, 1 H), 6.81 - 6.73 (m, 2 H), 6.72 - 6.65 (m, 3 H), 6.53 (d, *J* = 7.8 Hz, 1 H), 6.01 (t, *J* = 7.9 Hz, 1 H), 3.73 (s, 3 H), 2.49 - 2.40 (m, 4 H), 1.19 (d, *J* = 6.9 Hz, 6 H), 1.14 (d, *J* = 6.3 Hz, 10 H), 1.09 (t, *J* = 7.0 Hz, 3 H), 0.97 (d, *J* = 6.7 Hz, 5 H); **^{13}C NMR (175 MHz, DMSO-d$_6$) δ** = 189.5, 168.6, 159.9, 148.7, 146.5, 145.3, 145.1, 144.6, 142.4, 141.5, 137.2, 134.3, 133.6, 131.8, 131.8, 130.5, 130.4, 129.3, 129.2, 128.8, 127.7, 127.1, 126.3, 126.2, 125.0, 124.8, 124.3, 124.0, 123.7, 121.2, 120.7, 114.8, 113.2, 64.9, 55.5, 28.3, 28.2, 24.1, 23.8, 23.4, 15.2; **^{19}F NMR (375 MHz, DMSO-d$_6$) δ** = –77.74; **HRMS (ESI)** calcd for $C_{53}H_{54}AuClON_3^+$ $(M - OTf)^+$ 981.1157, found 981.1186.

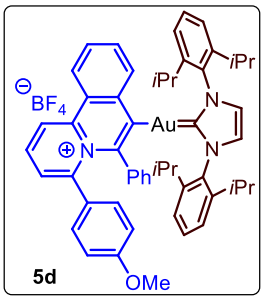


(5b): Yellow solid, 105 mg, 85% yield; ***Rf* =** 0.30 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (500 MHz, DMSO-d$_6$) δ** = 9.31 (d, *J* = 8.7 Hz, 1 H), 8.93 (d, *J* = 8.4 Hz, 1 H), 8.38 (t, *J* = 7.9 Hz, 1 H), 7.93 (s, 2 H), 7.87 (t, *J* = 7.6 Hz, 2 H), 7.80 (t, *J* = 7.6 Hz, 1 H), 7.68 (t, *J* = 7.8 Hz, 2 H), 7.63 (d, *J* = 7.0 Hz, 1 H), 7.57 (t, *J* = 7.5 Hz, 1 H), 7.42 (d, *J* = 7.8 Hz, 4 H), 7.40 - 7.34 (m, 2 H), 7.16 (d, *J* = 7.9 Hz, 1 H), 7.04 (s, 1 H), 6.74 (d, *J* = 7.5 Hz, 2 H), 6.65 (t, *J* = 7.4 Hz,

1 H), 6.24 (br. s., 2 H), 2.49 - 2.44 (m, 4 H), 1.17 (d, *J* = 6.9 Hz, 12 H), 1.05 (d, *J* = 6.9 Hz, 12 H); **^{13}C NMR (100 MHz, DMSO-d$_6$) δ** = 189.5, 169.3, 146.4, 145.2, 144.3, 142.1, 142.0, 141.9, 139.8, 138.4, 137.7, 136.9, 134.3, 133.8, 132.0, 130.4, 128.7, 127.9, 127.8, 127.3, 126.5, 126.3, 125.7, 125.1, 124.8, 124.3, 124.1, 123.4, 122.4, 122.3, 28.3, 23.9, 23.4; **^{19}F NMR (375 MHz, DMSO-d$_6$) δ** = –77.73; **HRMS (ESI)** calcd for $C_{53}H_{53}AuN_3S^+$ (M - OTf)$^+$ 972.3685, found 972.3691.

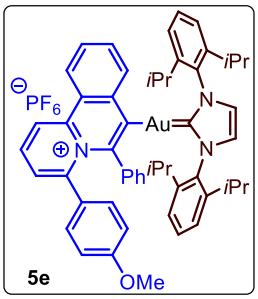


5c): Yellow solid, 120 mg, 89% yield; ***Rf* =** 0.20 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (500 MHz, DMSO-d$_6$) δ** = 9.20 (d, *J* = 8.4 Hz, 1 H), 8.89 (d, *J* = 8.5 Hz, 1 H), 8.34 (t, *J* = 7.9 Hz, 1 H), 7.92 (s, 2 H), 7.78 - 7.71 (m, 3 H), 7.62 (d, *J* = 7.2 Hz, 1 H), 7.52 (t, *J* = 7.6 Hz, 1 H), 7.45 (d, *J* = 7.9 Hz, 4 H), 7.13 (d, *J* = 7.6 Hz, 1 H), 6.84 - 6.78 (m, *J* = 8.7 Hz, 2 H), 6.73 (t, *J* = 7.4 Hz, 1 H), 6.65 - 6.60 (m, *J* = 8.9 Hz, 2 H), 6.55 (d, *J* = 7.3 Hz, 2 H), 6.41 - 6.33 (m, 2 H), 3.73 (s, 3 H), 2.49 - 2.43 (m, 4 H), 1.17 (d, *J* = 6.9 Hz, 12 H), 1.05 (d, *J* = 6.9 Hz, 12 H); **^{13}C NMR (175 MHz, DMSO-d$_6$) δ =** 190.1, 168.6, 160.2, 149.5, 146.7, 145.7, 144.8, 143.4, 142.1, 137.5, 134.9, 134.2, 132.1, 130.9, 130.9, 129.2, 128.9, 127.9, 127.8, 127.2, 126.7, 125.4, 125.3, 124.6, 123.9, 121.3, 120.0 (d, $J_{C\text{-}F}$ = 321.7 Hz), 114.2, 55.9, 28.7, 24.4, 23.9; **^{19}F NMR (375 MHz, DMSO-d$_6$) δ** = –78.70; **HRMS (ESI)** calcd for $C_{53}H_{55}AuON_3^+$ (M - OTf)$^+$ 946.4010, found 946.4005.

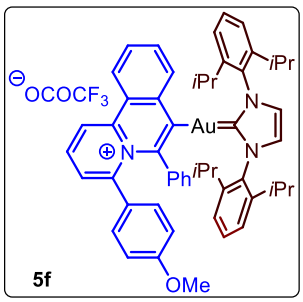


(5d): Yellow solid, 97 mg, 85% yield; ***Rf* =** 0.20 (CH_2Cl_2/MeOH = 95/05); **^{1}H NMR (500 MHz, DMSO-d$_6$) δ** = 9.20 (d, *J* = 8.2 Hz, 1 H), 8.89 (d, *J* = 8.5 Hz, 1 H), 8.34 (t, *J* = 7.9 Hz, 1 H), 7.92 (s, 2 H), 7.82 - 7.71 (m, 3 H), 7.62 (d, *J* = 7.0 Hz, 1 H), 7.52 (t, *J* = 7.6 Hz, 1 H),

7.46 (d, *J* = 7.8 Hz, 4 H), 7.13 (d, *J* = 7.9 Hz, 1 H), 6.86 - 6.78 (m, *J* = 8.7 Hz, 2 H), 6.73 (t, *J* = 7.4 Hz, 1 H), 6.68 - 6.59 (m, *J* = 8.7 Hz, 2 H), 6.55 (d, *J* = 7.3 Hz, 2 H), 6.37 (t, *J* = 7.6 Hz, 2 H), 3.73 (s, 3 H), 2.49 - 2.44 (m, 4 H), 1.17 (d, *J* = 6.9 Hz, 12 H), 1.05 (d, *J* = 6.9 Hz, 12 H); **^{13}C NMR (175 MHz, DMSO-d$_6$) δ =** 189.7, 168.1, 159.7, 149.1, 146.2, 145.2, 144.3, 142.9, 141.7, 137.0, 134.4, 133.7, 131.7, 130.5, 130.4, 128.8, 128.5, 127.4, 127.4, 126.7, 126.2, 124.9, 124.8, 124.1, 123.5, 120.8, 113.7, 55.4, 28.3, 23.9, 23.4; **^{11}B NMR (128 MHz, DMSO-d$_6$) δ** = –1.29; **^{19}F NMR (375 MHz, DMSO-d$_6$) δ** = –148.30; **HRMS (ESI)** calcd for $C_{53}H_{55}AuON_3^+$ (M - OTf)$^+$ 946.4018, found 946.4005.

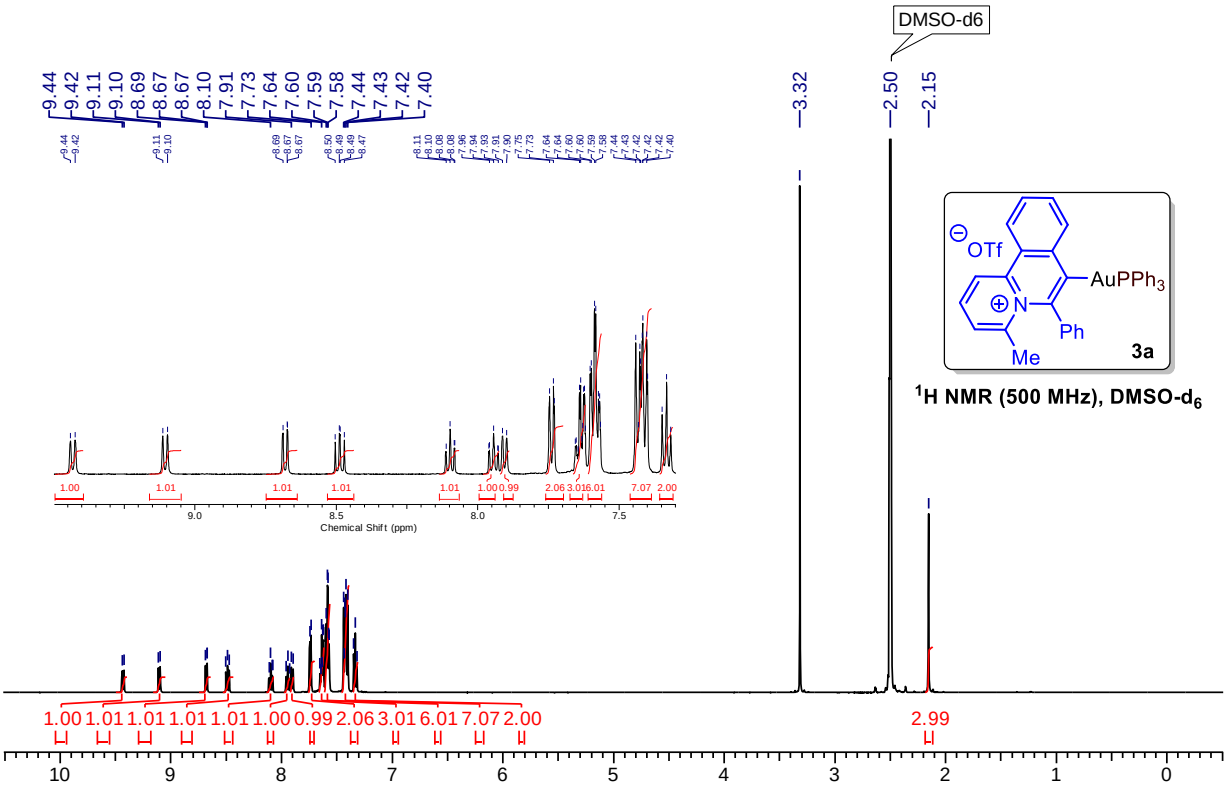


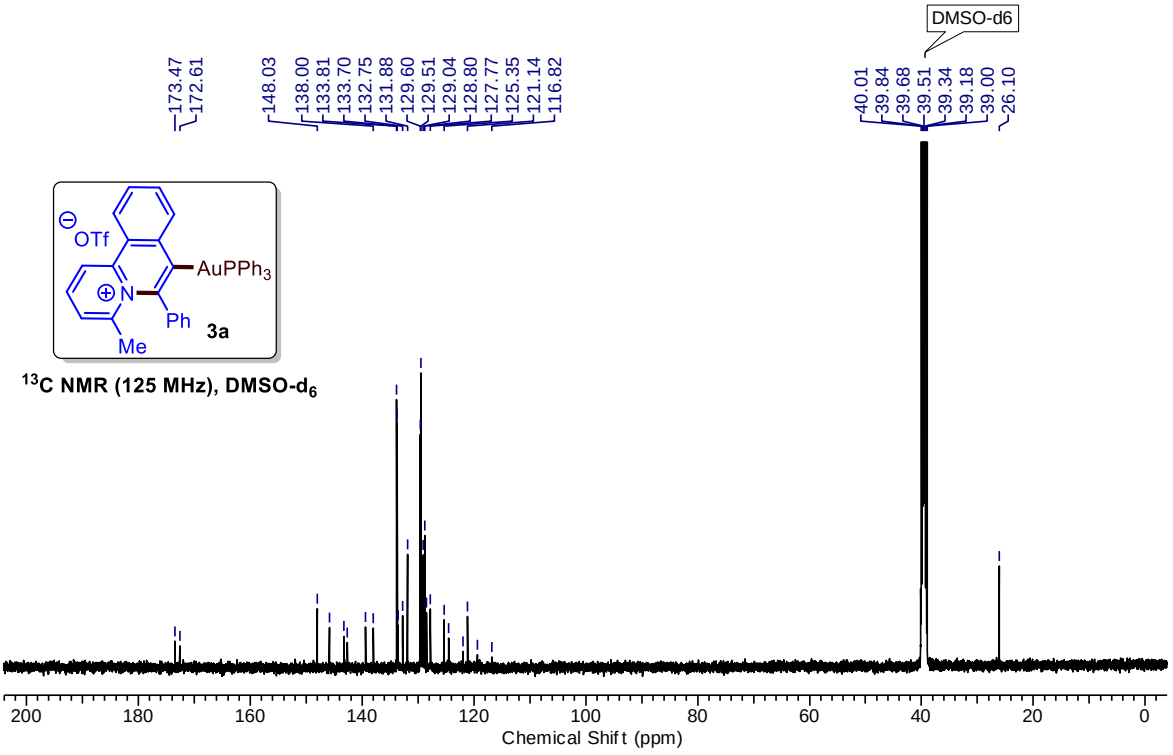
(5e): Yellow solid, 101 mg, 84% yield; ***Rf* =** 0.20 (CH_2Cl_2/MeOH = 93/07); **^{1}H NMR (500 MHz, DMSO-d$_6$) δ** = 9.20 (d, *J* = 8.5 Hz, 1 H), 8.89 (d, *J* = 8.2 Hz, 1 H), 8.34 (t, *J* = 7.9 Hz, 1 H), 7.92 (s, 2 H), 7.79 - 7.72 (m, 3 H), 7.62 (d, *J* = 7.0 Hz, 1 H), 7.52 (t, *J* = 7.6 Hz, 1 H), 7.45 (d, *J* = 7.8 Hz, 4 H), 7.13 (d, *J* = 7.9 Hz, 1 H), 6.86 - 6.79 (m, *J* = 8.7 Hz, 2 H), 6.73 (t, *J* = 7.4 Hz, 1 H), 6.66 - 6.58 (m, *J* = 8.7 Hz, 2 H), 6.55 (d, *J* = 7.3 Hz, 2 H), 6.37 (t, *J* = 7.6 Hz, 2 H), 3.73 (s, 3 H), 2.49 - 2.45 (m, 4 H), 1.17 (d, *J* = 6.7 Hz, 12 H), 1.05 (d, *J* = 6.9 Hz, 12 H); **^{13}C NMR (175 MHz, DMSO-d$_6$) δ =** 189.7, 168.1, 159.7, 149.7, 149.1, 146.2, 145.2, 144.3, 142.9, 141.7, 137.0, 134.4, 133.7, 131.7, 130.5, 130.4, 128.8, 128.4, 127.4, 127.4, 126.7, 126.2, 124.9, 124.8, 124.1, 123.4, 120.8, 115.6, 113.7, 55.4, 28.3, 23.9, 23.4; **^{31}P NMR (162 MHz, DMSO-d$_6$) δ** = -9.10, -14.98, -20.85; **^{19}F NMR (375 MHz, DMSO-d$_6$) δ** = –76.97, –79.50; **HRMS (ESI)** calcd for $C_{53}H_{55}AuON_3^+$ (M - OTf)$^+$ 946.4013, found 946.4005.

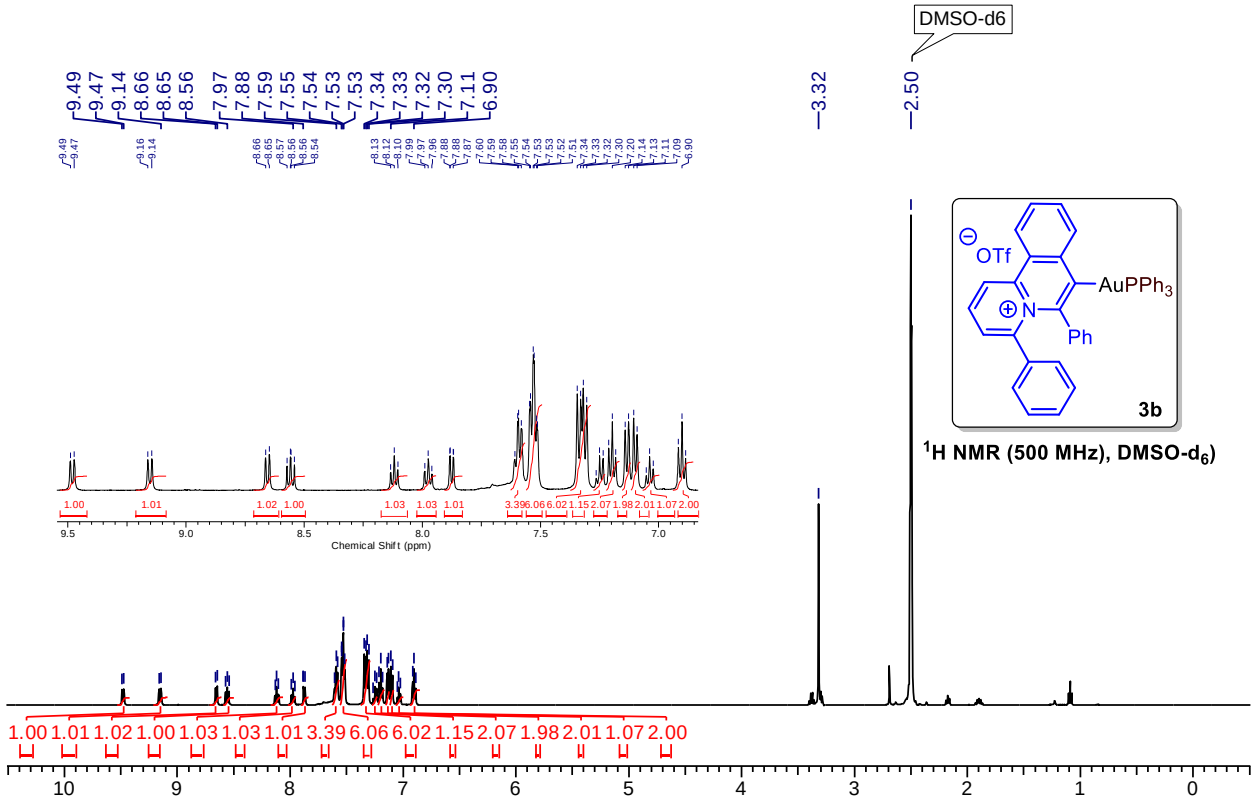


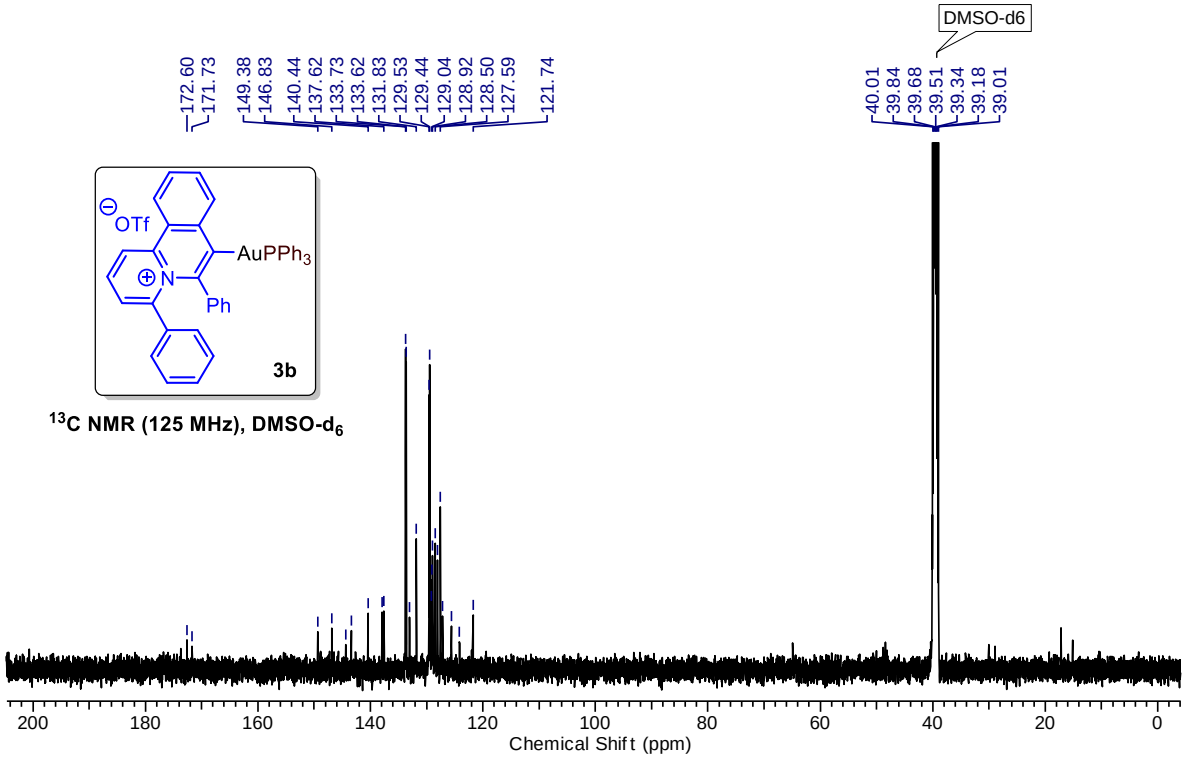
(5f): Yellow solid, 92 mg, 79% yield; ***Rf* =** 0.20 (CH_2Cl_2/MeOH = 93/07); **^{1}H NMR (500 MHz**, **DMSO-d$_6$) δ** = 9.21 (d, *J* = 8.7 Hz, 1 H), 8.89 (d, *J* = 8.4 Hz, 1 H), 8.34 (t, *J* = 7.9 Hz, 1 H), 7.92 (s, 2 H), 7.78 - 7.72 (m, 3 H), 7.62 (d, *J* = 7.2 Hz, 1 H), 7.52 (t, *J* = 7.6 Hz, 1 H), 7.45 (d, *J* = 7.8 Hz, 4 H), 7.13 (d, *J* = 7.9 Hz, 1 H), 6.84 - 6.79 (m, *J* = 8.5 Hz, 2 H), 6.73 (t, *J* = 7.4 Hz, 1 H), 6.65 - 6.59 (m, *J* = 8.7 Hz, 2 H), 6.55 (d, *J* = 7.3 Hz, 2 H), 6.37 (t, *J* = 7.6 Hz, 2 H), 3.73 (s, 3 H), 2.49 - 2.45 (m, 4 H), 1.17 (d, *J* = 6.7 Hz, 12 H), 1.05 (d, *J* = 6.9 Hz, 12 H); **^{13}C NMR (175 MHz**, **DMSO-d$_6$) δ =** 189.7, 168.1, 159.7, 157.6 (q, $J_{C\text{-}F}$ = 30.5 Hz), 149.7, 149.1, 146.2, 145.2, 144.3, 142.9, 141.7, 137.0, 134.4, 133.7, 131.7, 130.5, 130.4, 128.7, 128.4, 127.4, 127.4, 126.7, 126.2, 124.9, 124.8, 124.1, 123.4, 120.8, 117.4, 115.6, 113.7, 55.4, 28.3, 23.9, 23.4; **^{19}F NMR (375 MHz**, **DMSO-d$_6$) δ** = –73.40; **HRMS (ESI)** calcd for $C_{53}H_{55}AuON_3^+$ (M - OTf)$^+$946.4009, found 946.4005.

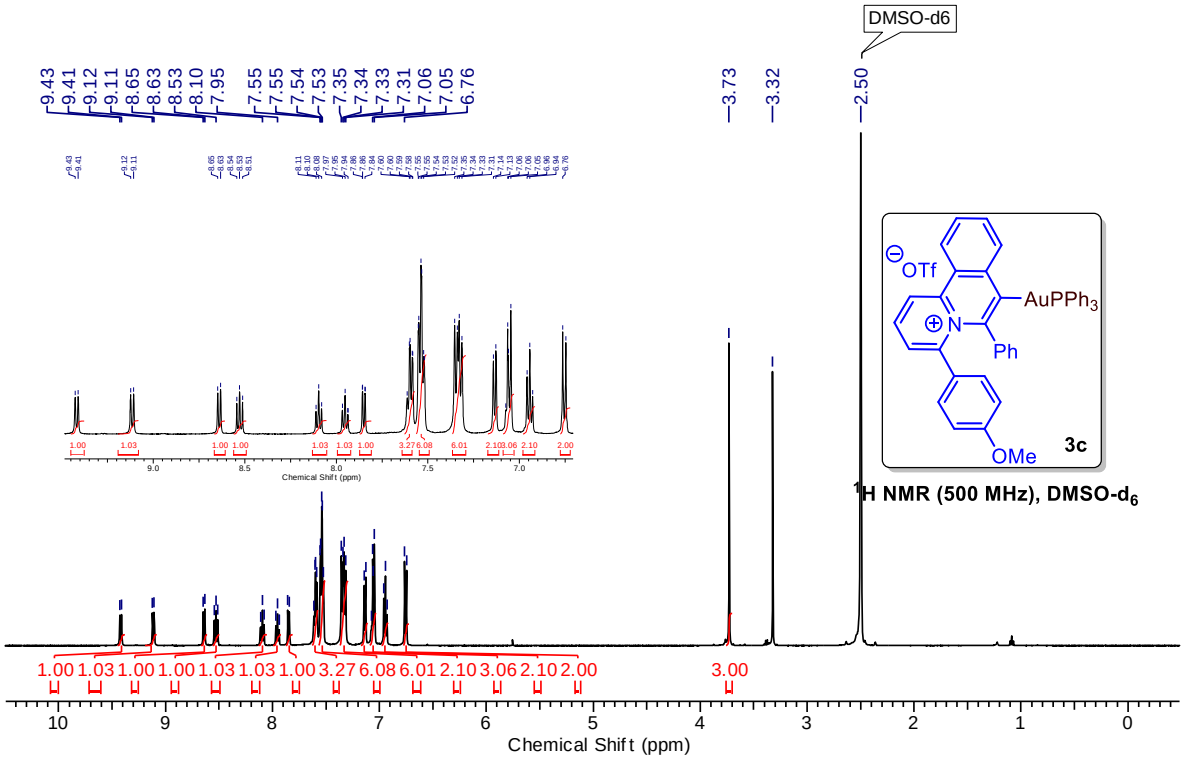
5 NMR spectra

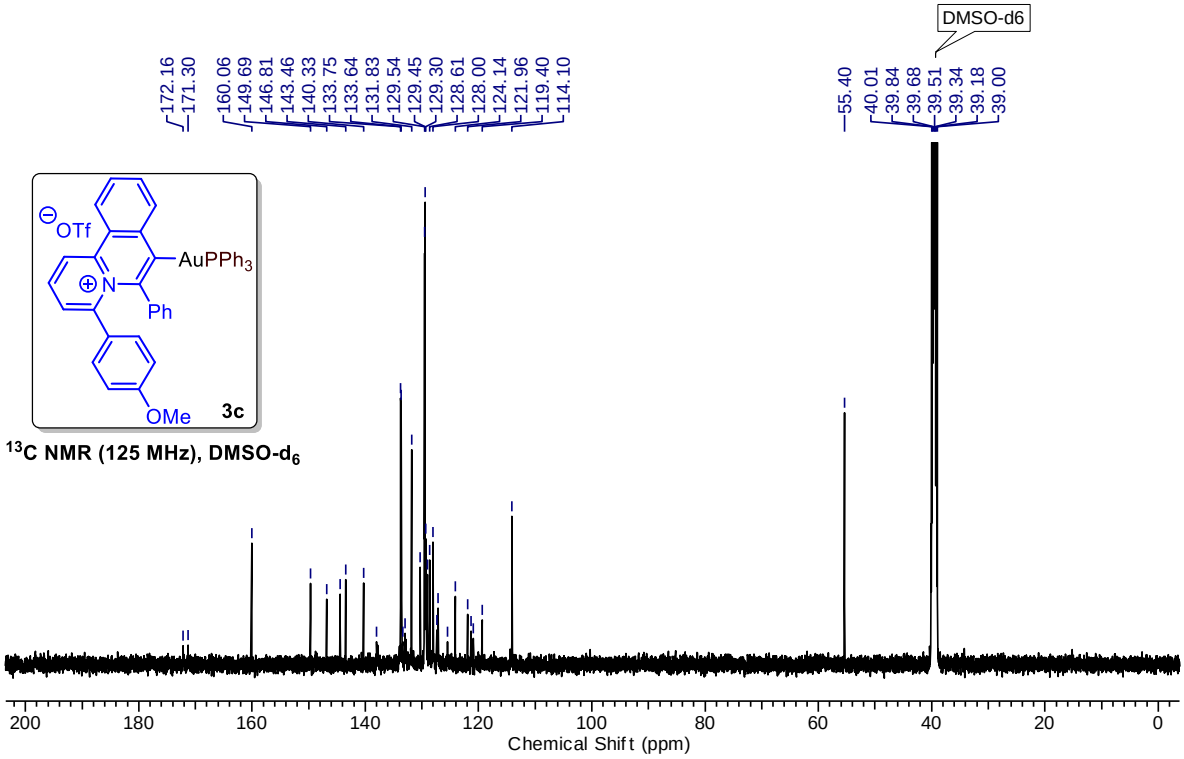


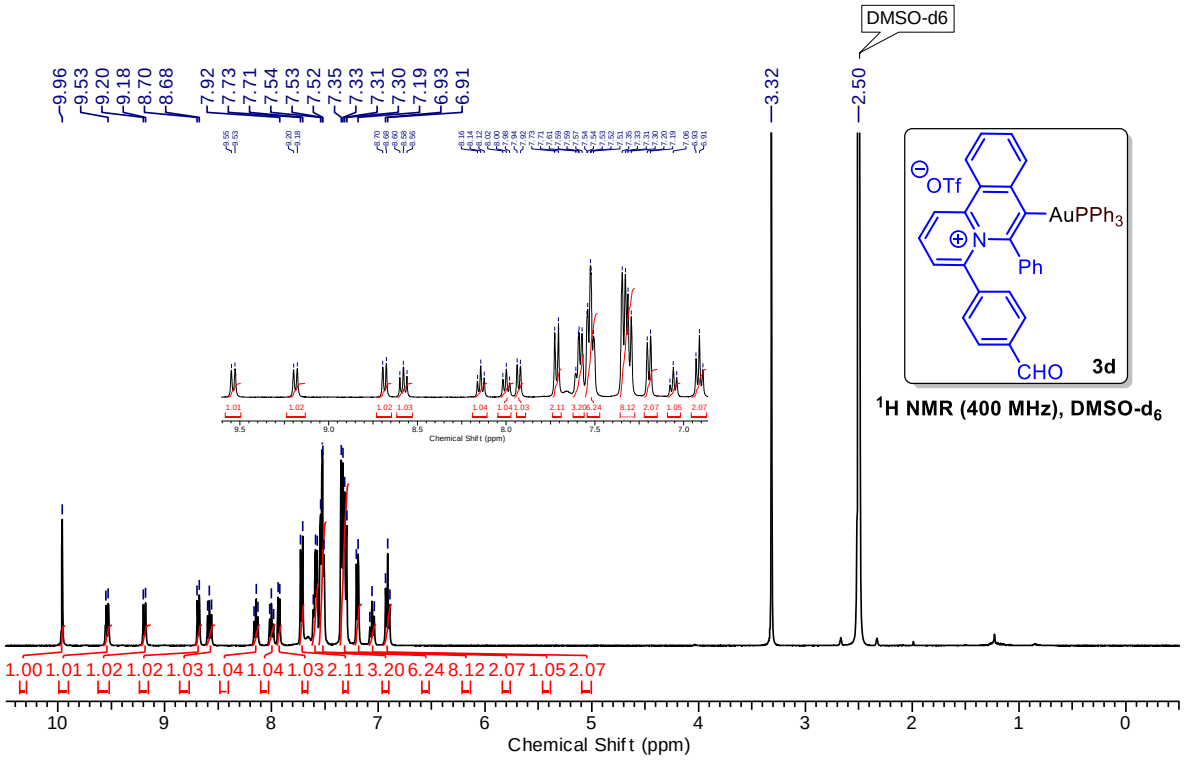


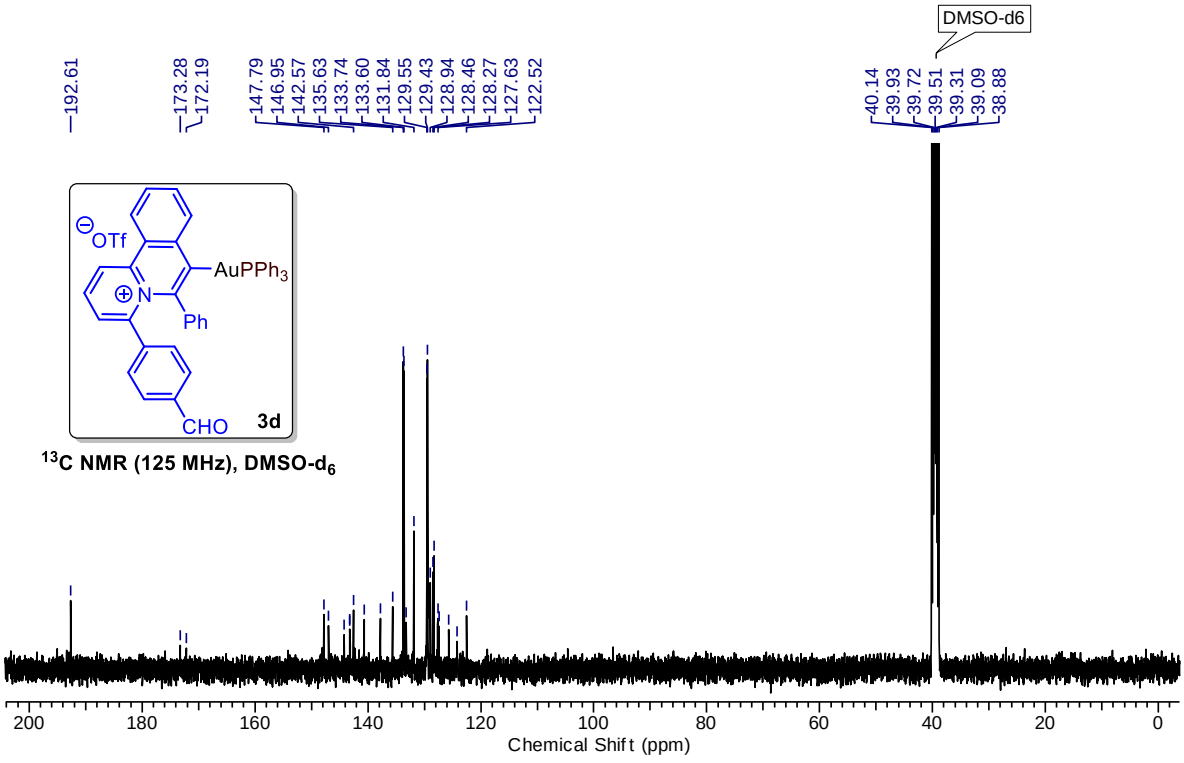

DMSO-d6
9.49
9.47
9.14
8.66
8.65
8.56
7.97
7.88
7.59
7.55
7.54
7.53
7.53
7.34
7.33
7.32
7.30
7.11
6.90
3.32
2.50
OTf
AuPPh3
N
Ph
3b
1H NMR (500 MHz), DMSO-d6)
1.00 1.01 1.02 1.00 1.03 1.03 1.01 3.39 6.06 6.02 1.15 2.07 1.98 2.01 1.07 2.00
Chemical Shift (ppm)

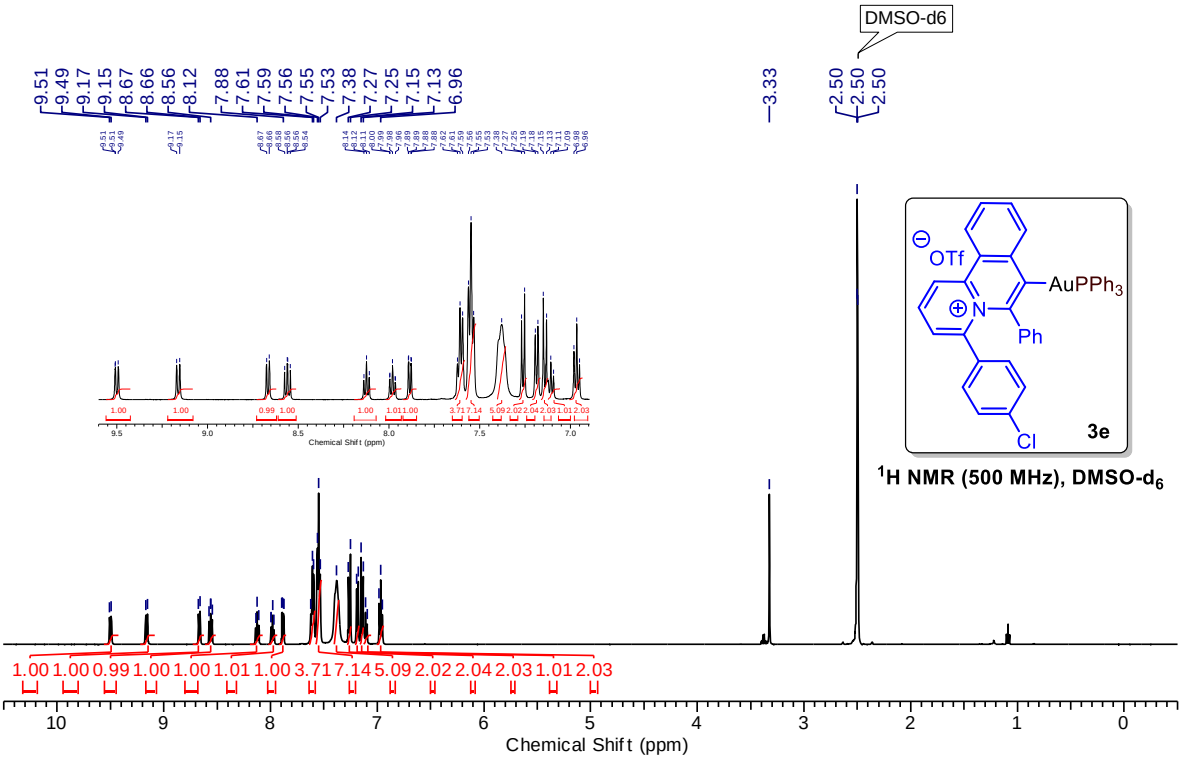

DMSO-d6
172.60
171.73
149.38
146.83
140.44
137.62
133.73
133.62
131.83
129.53
129.44
129.04
128.92
128.50
127.59
121.74
40.01
39.84
39.68
39.51
39.34
39.18
39.01
OTf
AuPPh3
N
Ph
3b
13C NMR (125 MHz), DMSO-d6
Chemical Shift (ppm)

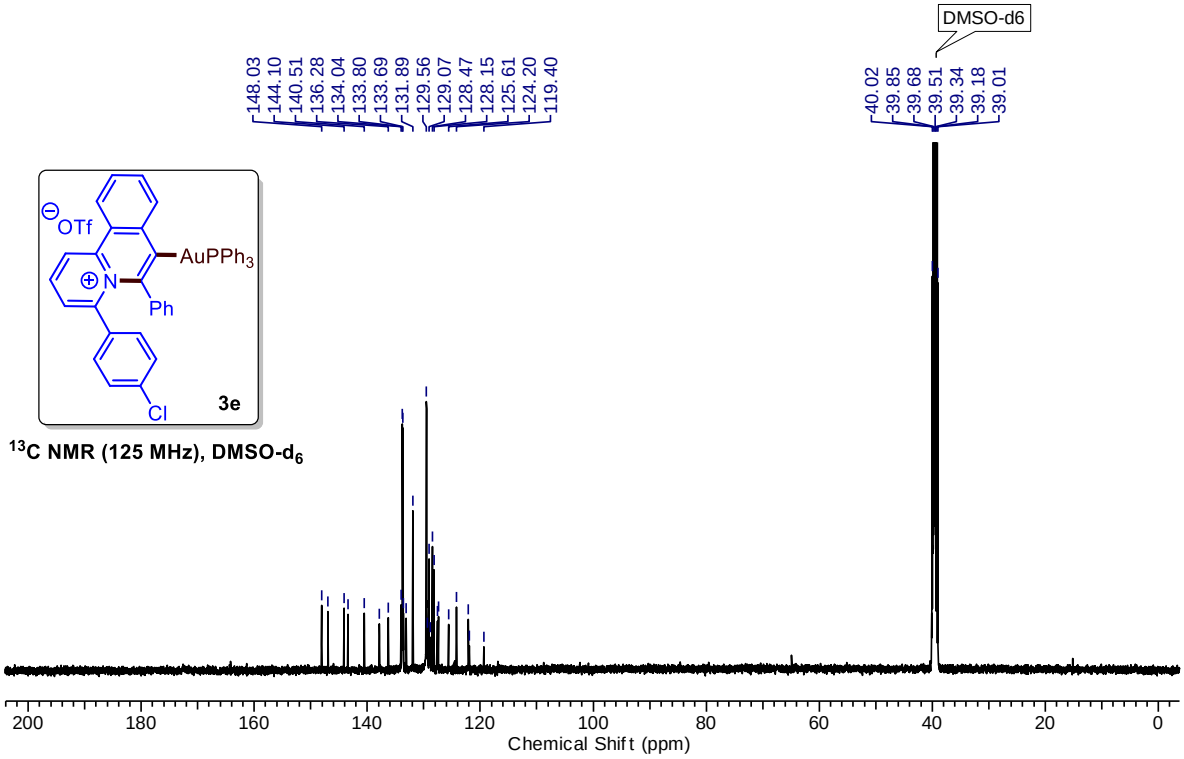

DMSO-d6
9.43
9.41
9.12
9.11
8.65
8.63
8.53
8.10
7.95
7.55
7.55
7.54
7.53
7.35
7.34
7.33
7.31
7.06
7.05
6.76
3.73
3.32
2.50
OTf
AuPPh3
N
Ph
OMe
3c
1H NMR (500 MHz), DMSO-d6
1.00 1.03 1.00 1.00 1.03 1.03 1.00 3.27 6.08 6.01 2.10 3.06 2.10 2.00
3.00
Chemical Shift (ppm)

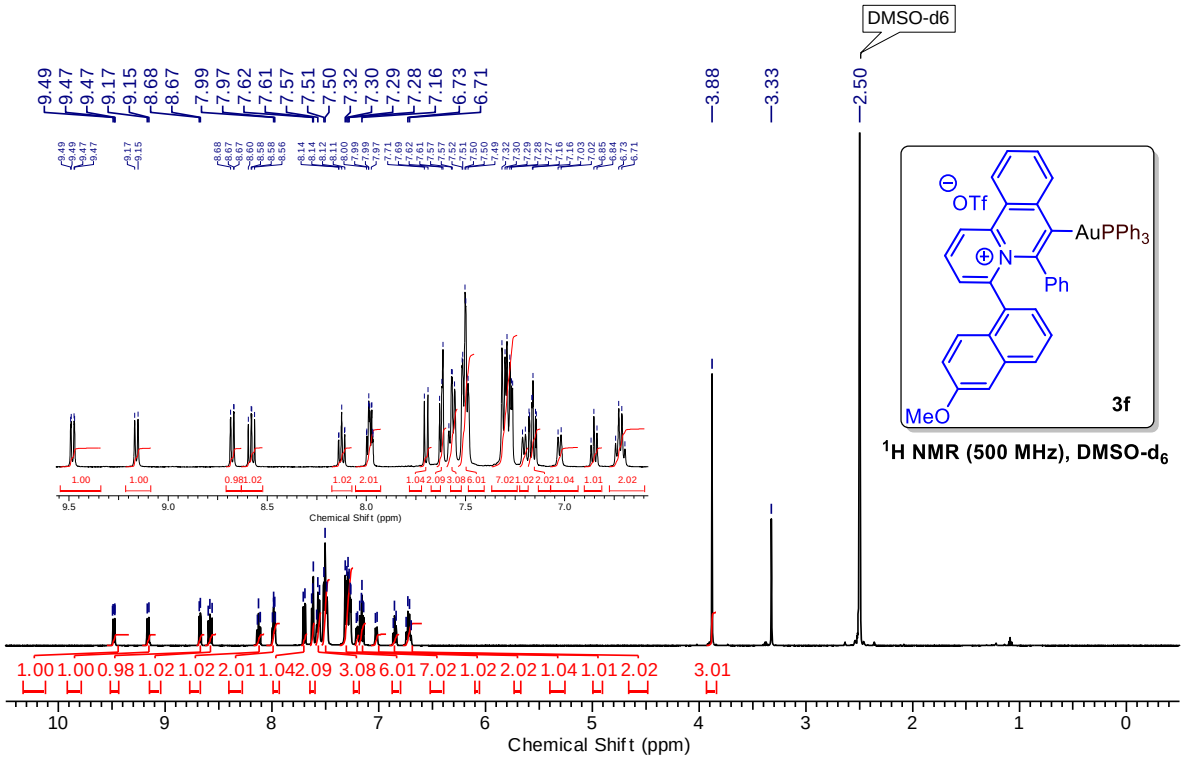

DMSO-d6
172.16
171.30
160.06
149.69
146.81
143.46
140.33
133.75
133.64
131.83
129.54
129.45
129.30
128.61
128.00
124.14
121.96
119.40
114.10
55.40
40.01
39.84
39.68
39.51
39.34
39.18
39.00
OTf
AuPPh3
N
Ph
OMe
3c
13C NMR (125 MHz), DMSO-d6
Chemical Shift (ppm)


DMSO-d6
9.96
9.53
9.20
9.18
8.70
8.68
7.92
7.73
7.71
7.54
7.53
7.52
7.35
7.33
7.31
7.30
7.19
6.93
6.91
3.32
2.50
OTf
AuPPh3
N
Ph
CHO
3d
1H NMR (400 MHz), DMSO-d6
1.00 1.01 1.02 1.02 1.03 1.04 1.04 1.03 2.11 3.20 6.24 8.12 2.07 1.05 2.07
Chemical Shift (ppm)

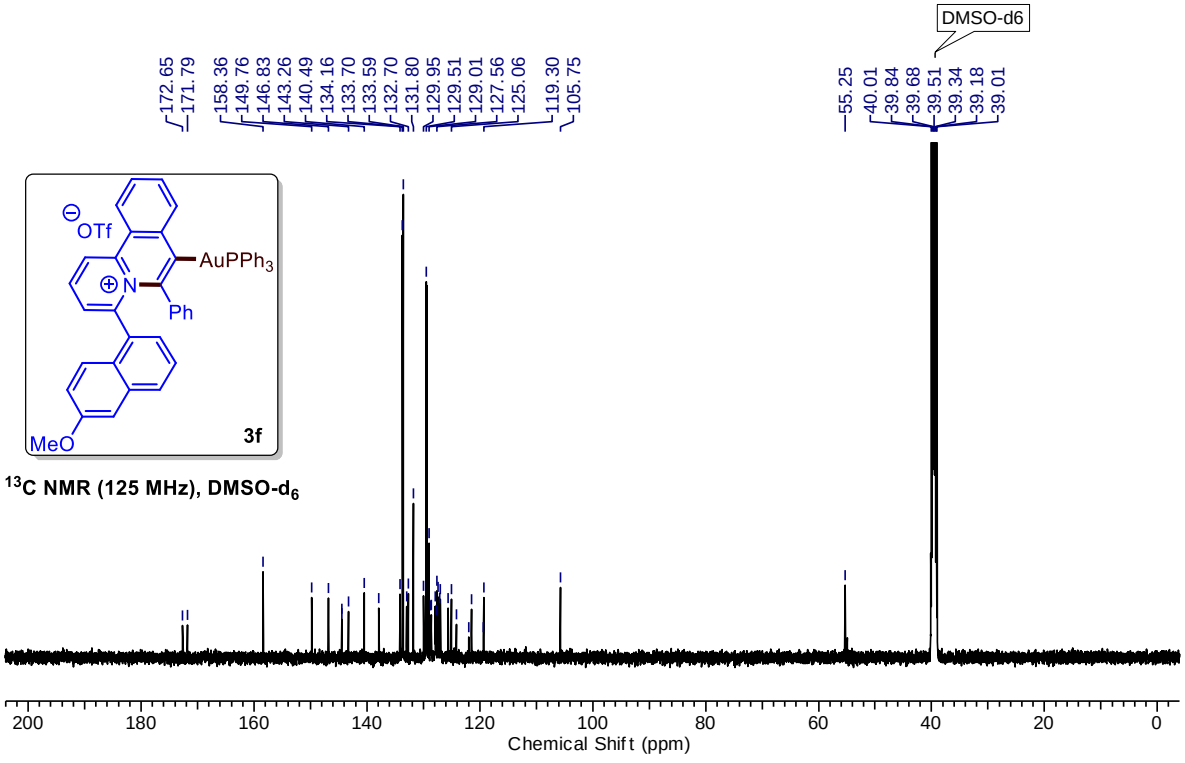

DMSO-d6
192.61
173.28
172.19
147.79
146.95
142.57
135.63
133.74
133.60
131.84
129.55
129.43
128.94
128.46
128.27
127.63
122.52
40.14
39.93
39.72
39.51
39.31
39.09
38.88
OTf
AuPPh3
N
Ph
CHO
3d
13C NMR (125 MHz), DMSO-d6
Chemical Shift (ppm)


DMSO-d6
9.51
9.49
9.17
9.15
8.67
8.66
8.56
8.12
7.88
7.61
7.59
7.56
7.55
7.53
7.38
7.27
7.25
7.15
7.13
6.96
3.33
2.50
2.50
2.50
OTf
AuPPh3
N
Ph
Cl
3e
1H NMR (500 MHz), DMSO-d6
1.00 1.00 0.99 1.00 1.00 1.01 1.00 3.71 7.14 5.09 2.02 2.04 2.03 1.01 2.03
Chemical Shift (ppm)

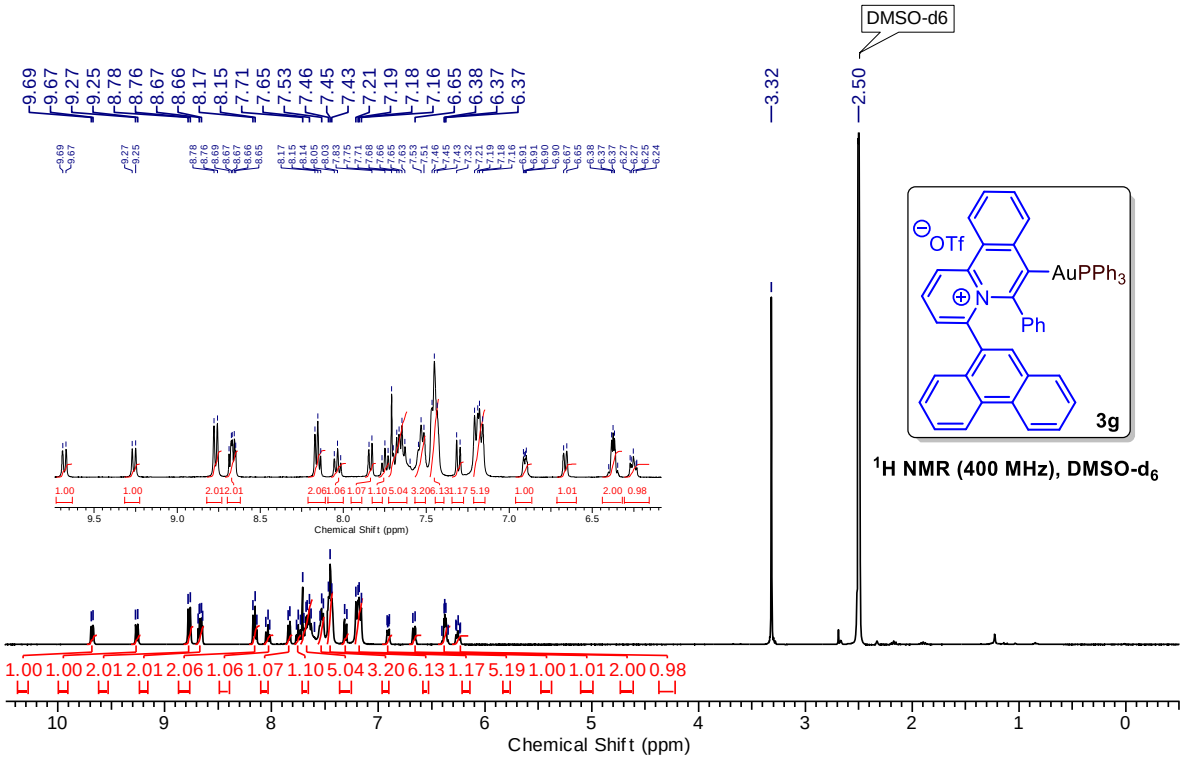

DMSO-d6
148.03
144.10
140.51
136.28
134.04
133.80
133.69
131.89
129.56
129.07
128.47
128.15
125.61
124.20
119.40
40.02
39.85
39.68
39.51
39.34
39.18
39.01
OTf
AuPPh3
N
Ph
Cl
3e
13C NMR (125 MHz), DMSO-d6
Chemical Shift (ppm)

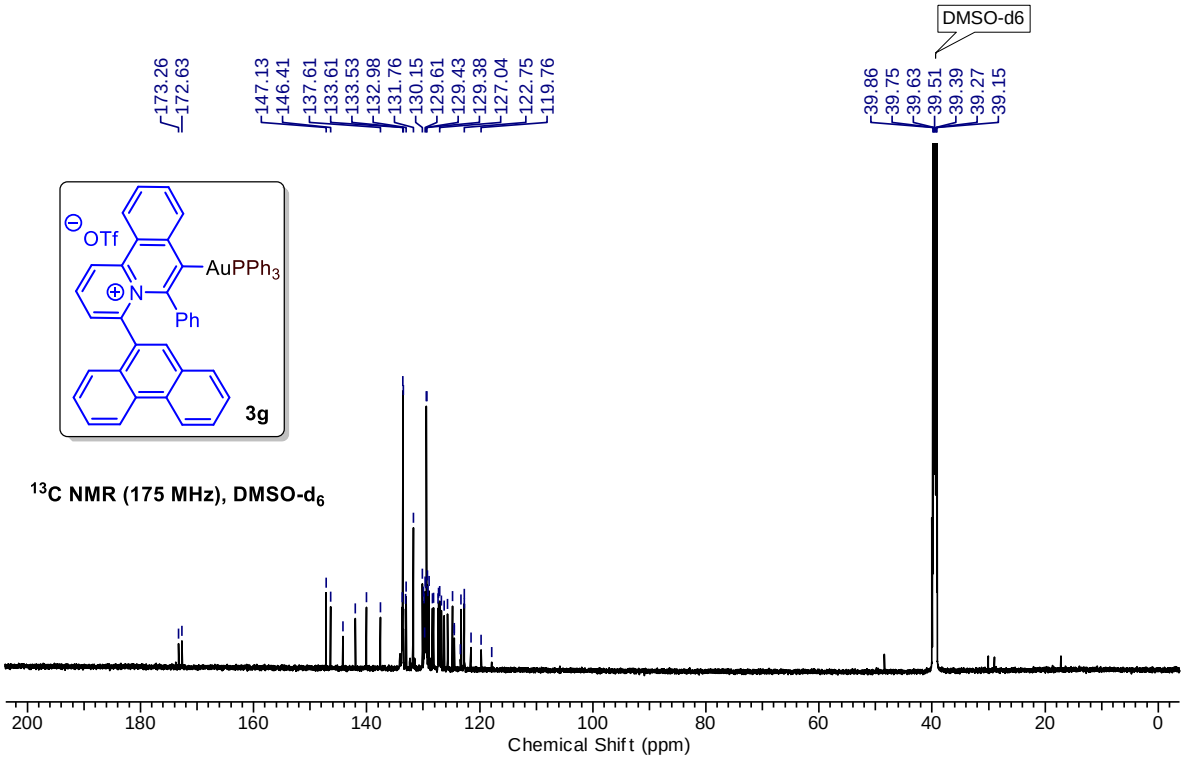


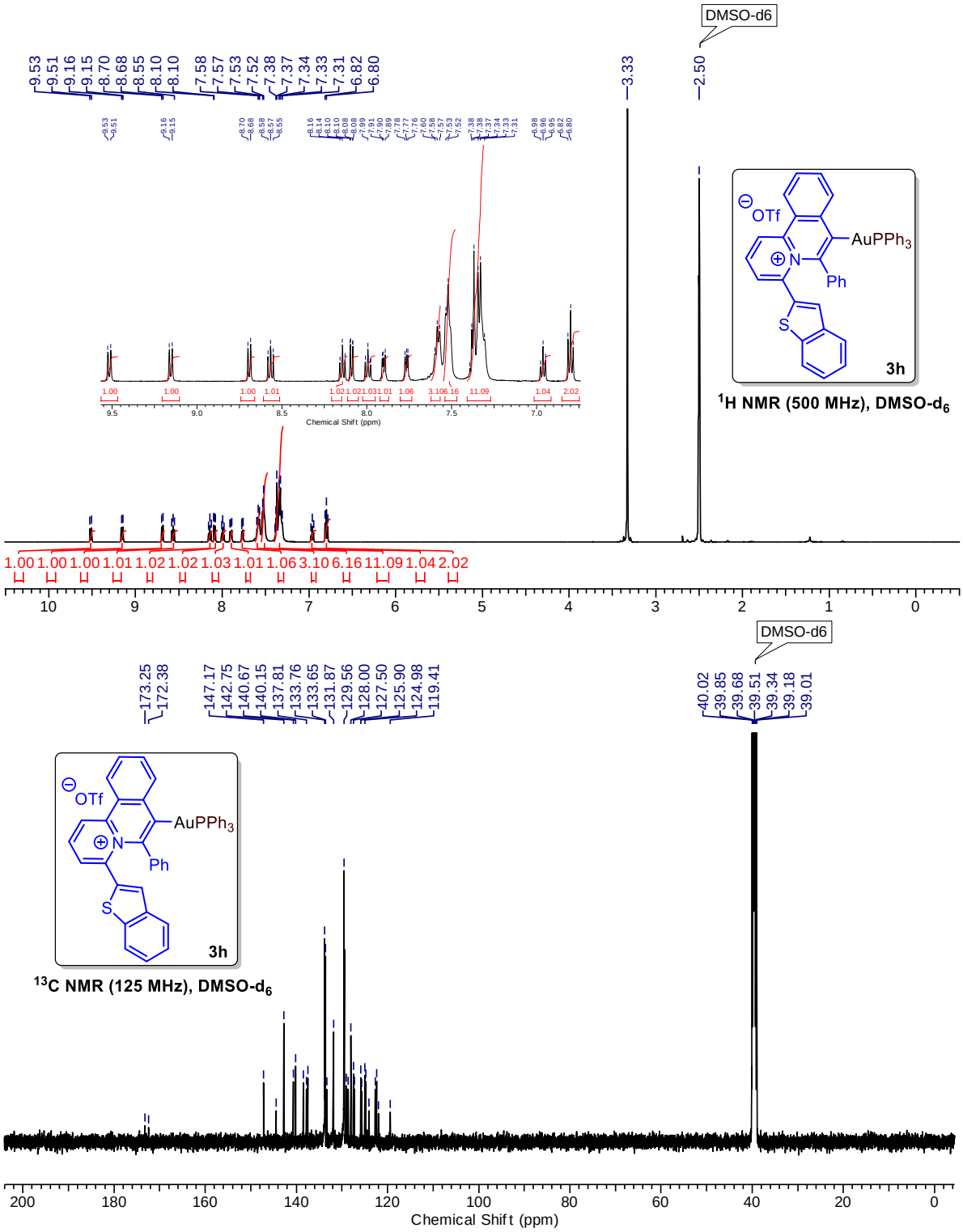
^{1}H NMR (500 MHz), DMSO-d$_6$

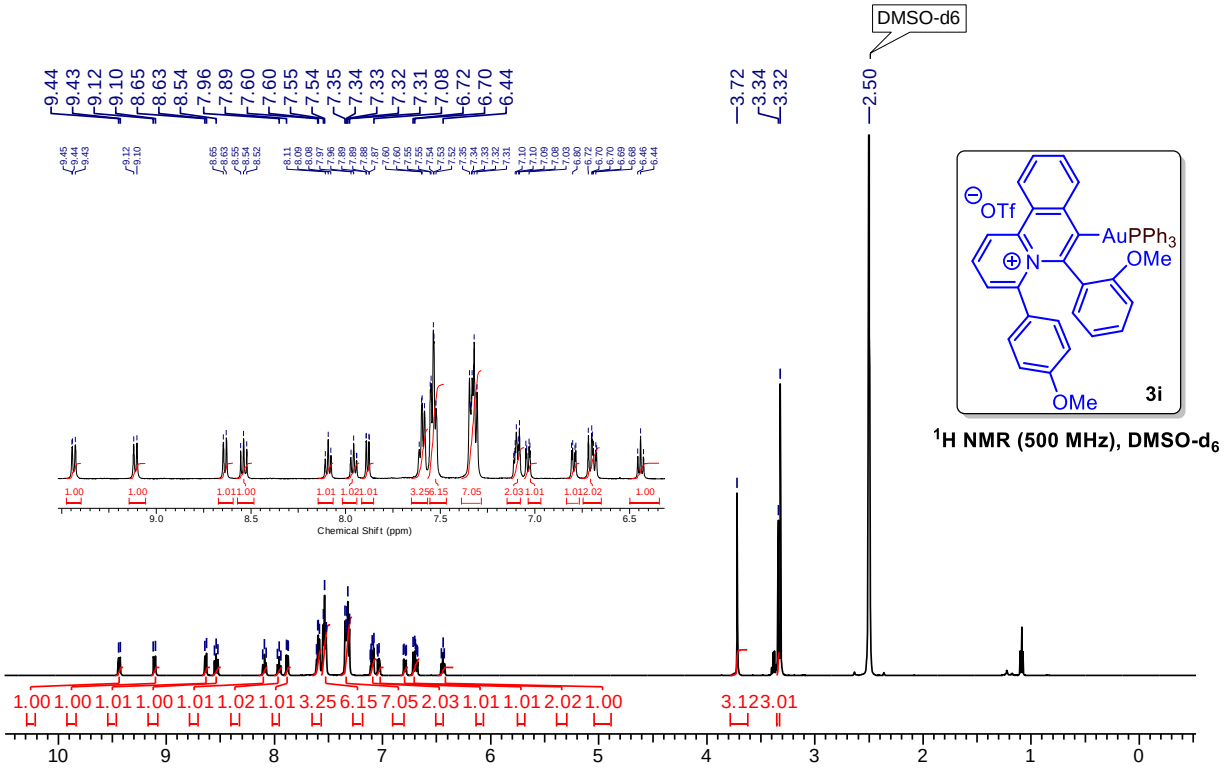


^{13}C NMR (125 MHz), DMSO-d$_6$

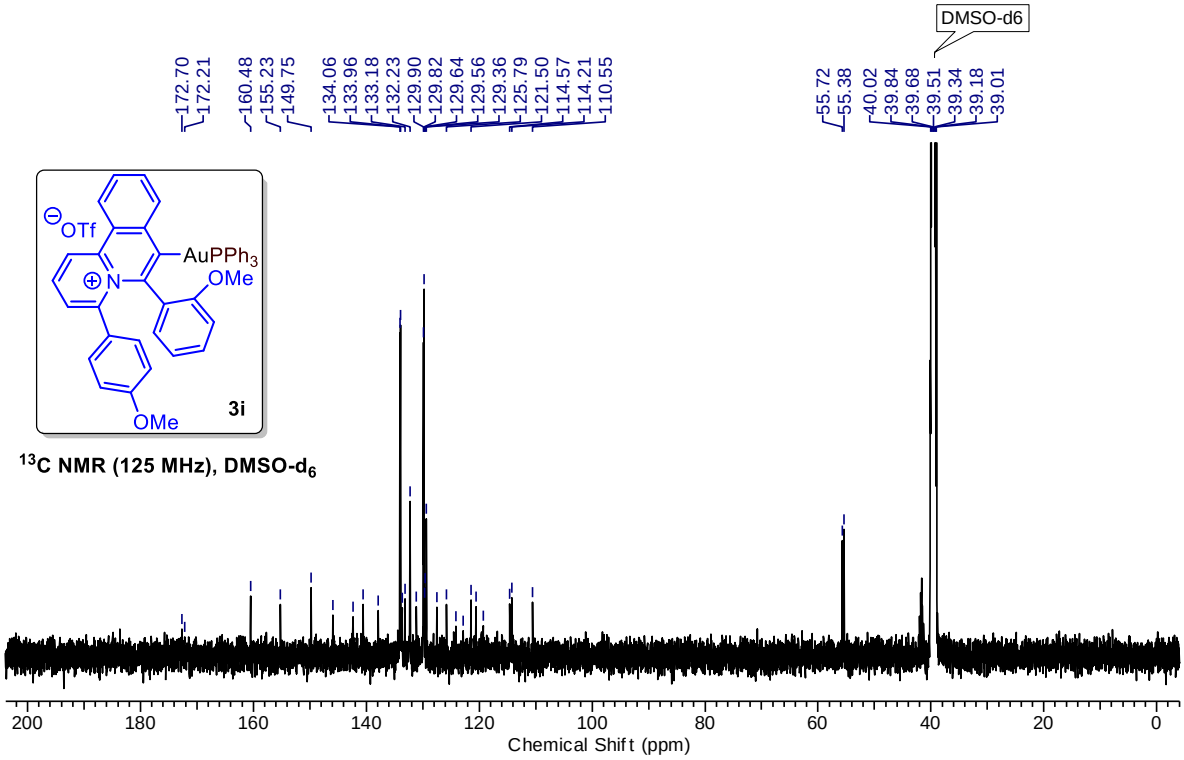

DMSO-d6
3.32
2.50
OTf
AuPPh3
Ph
3g
1H NMR (400 MHz), DMSO-d6
Chemical Shift (ppm)


DMSO-d6
OTf
AuPPh3
Ph
3g
13C NMR (175 MHz), DMSO-d6
Chemical Shift (ppm)

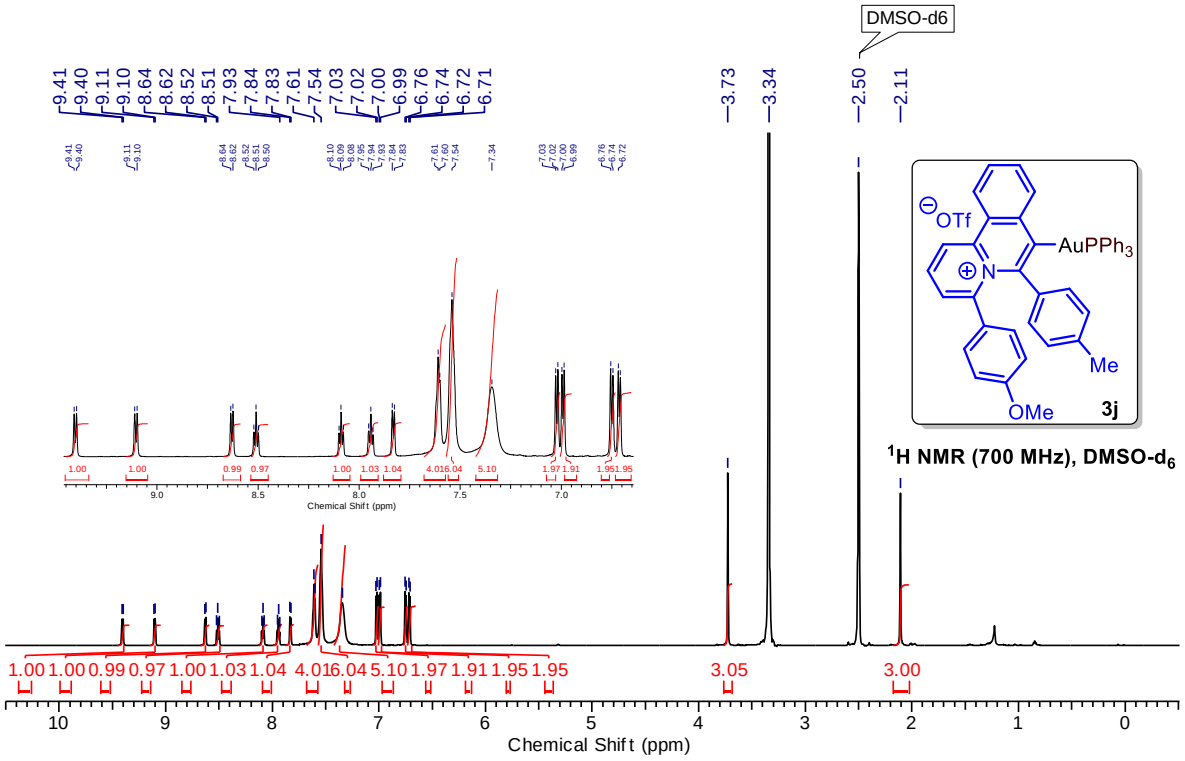

DMSO-d6
9.53
9.51
9.16
9.15
8.70
8.68
8.55
8.10
8.10
7.58
7.57
7.53
7.52
7.38
7.37
7.34
7.33
7.31
6.82
6.80
3.33
2.50
OTf
AuPPh3
Ph
S
3h
1H NMR (500 MHz), DMSO-d6
1.00 1.00 1.00 1.01 1.02 1.02 1.03 1.01 1.06 3.10 6.16 11.09 1.04 2.02
Chemical Shift (ppm)
DMSO-d6
173.25
172.38
147.17
142.75
140.67
140.15
137.81
133.76
133.65
131.87
129.56
128.00
127.50
125.90
124.98
119.41
40.02
39.85
39.68
39.51
39.34
39.18
39.01
13C NMR (125 MHz), DMSO-d6
Chemical Shift (ppm)

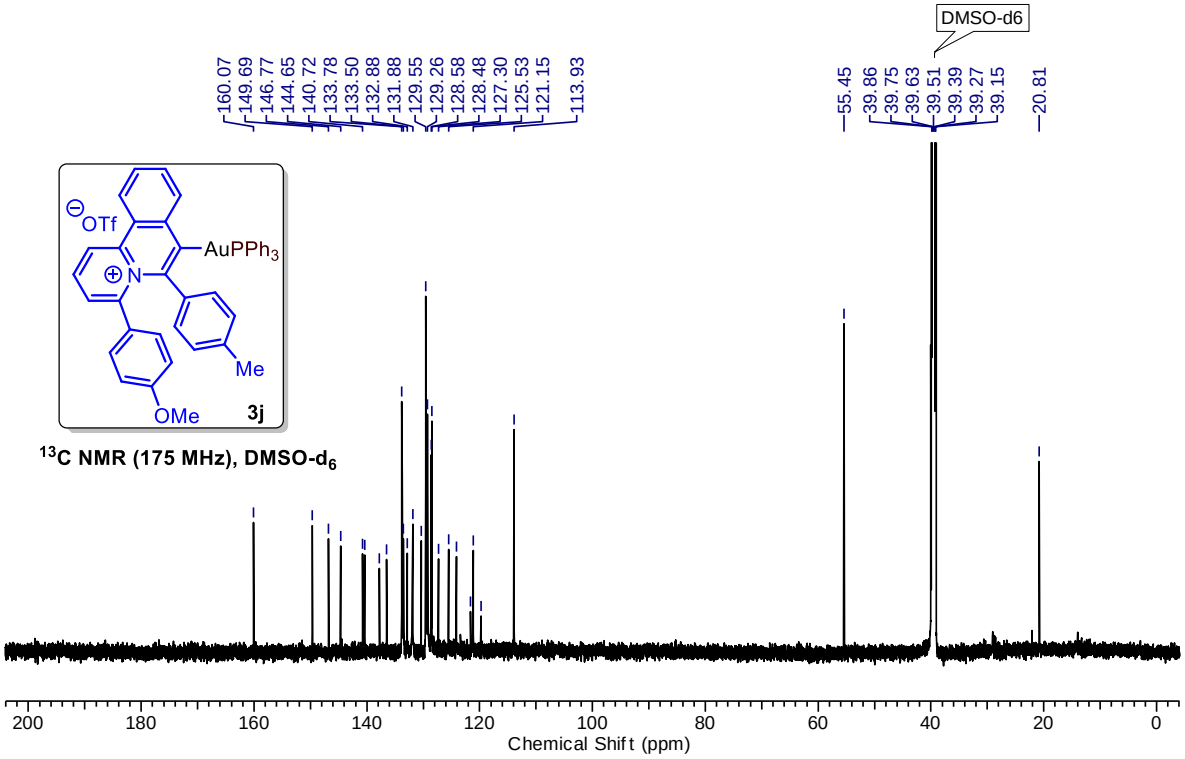


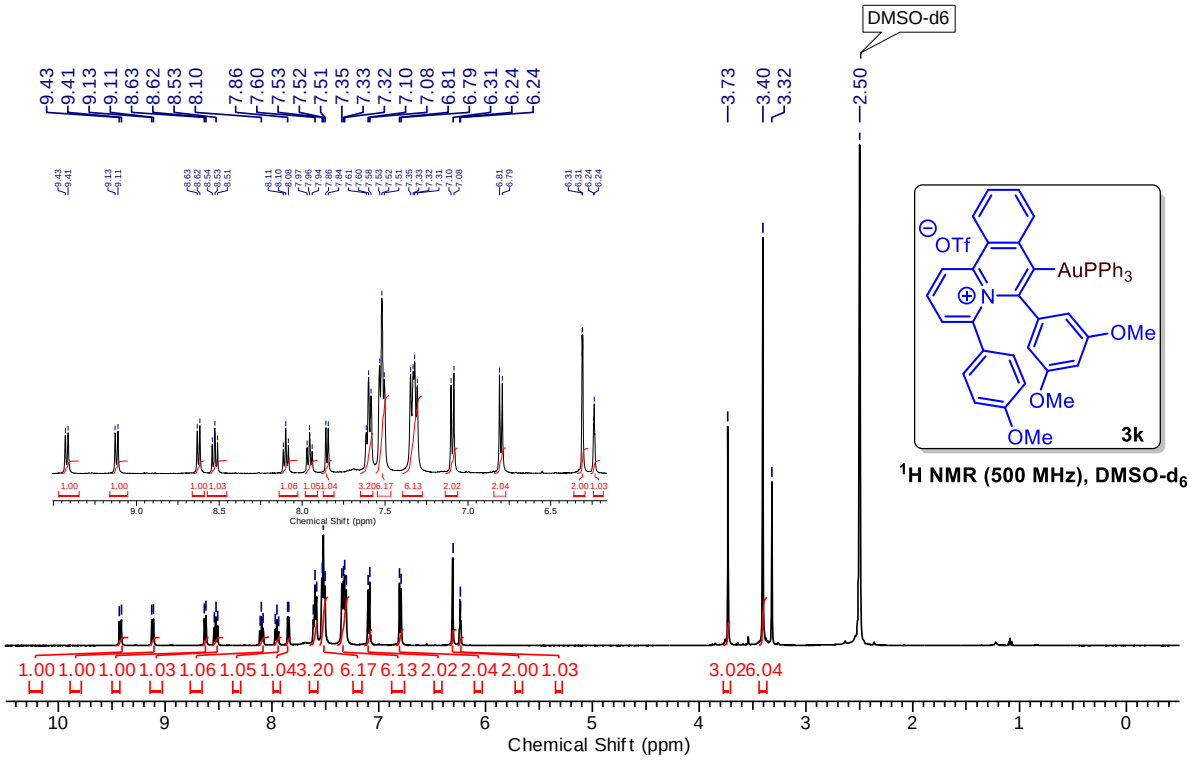
^{1}H NMR (500 MHz), DMSO-d_6

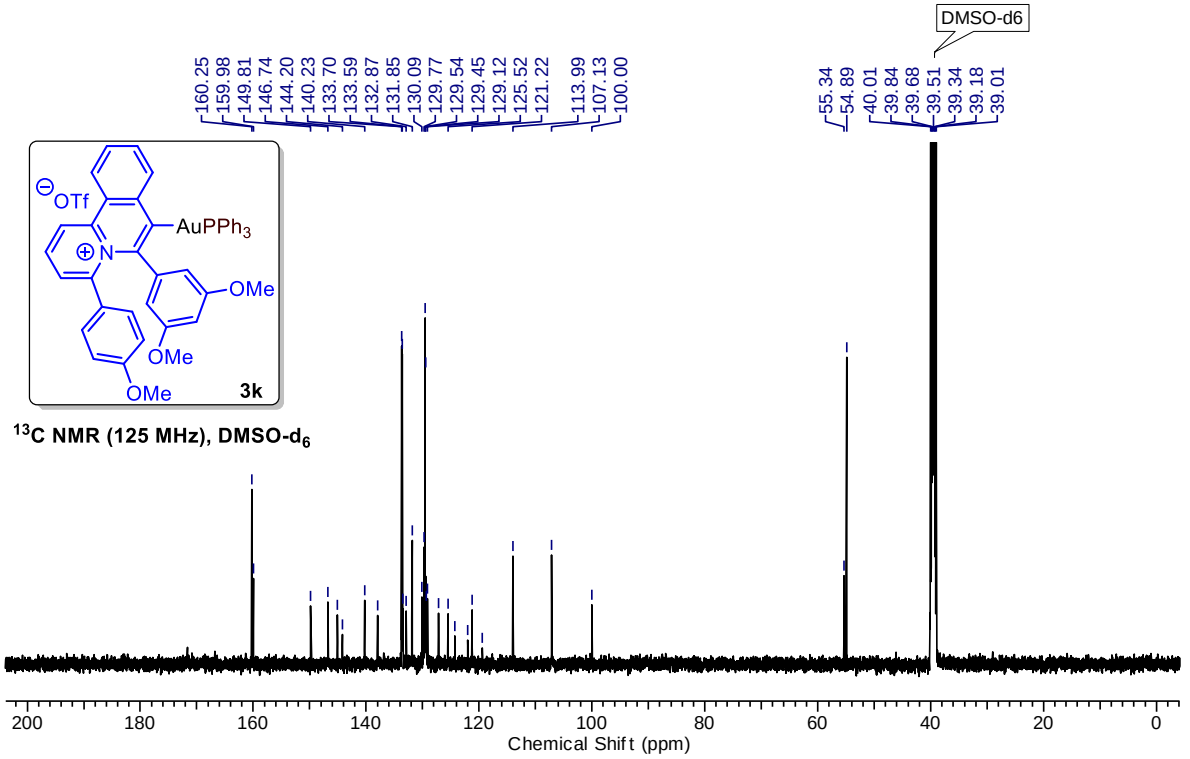


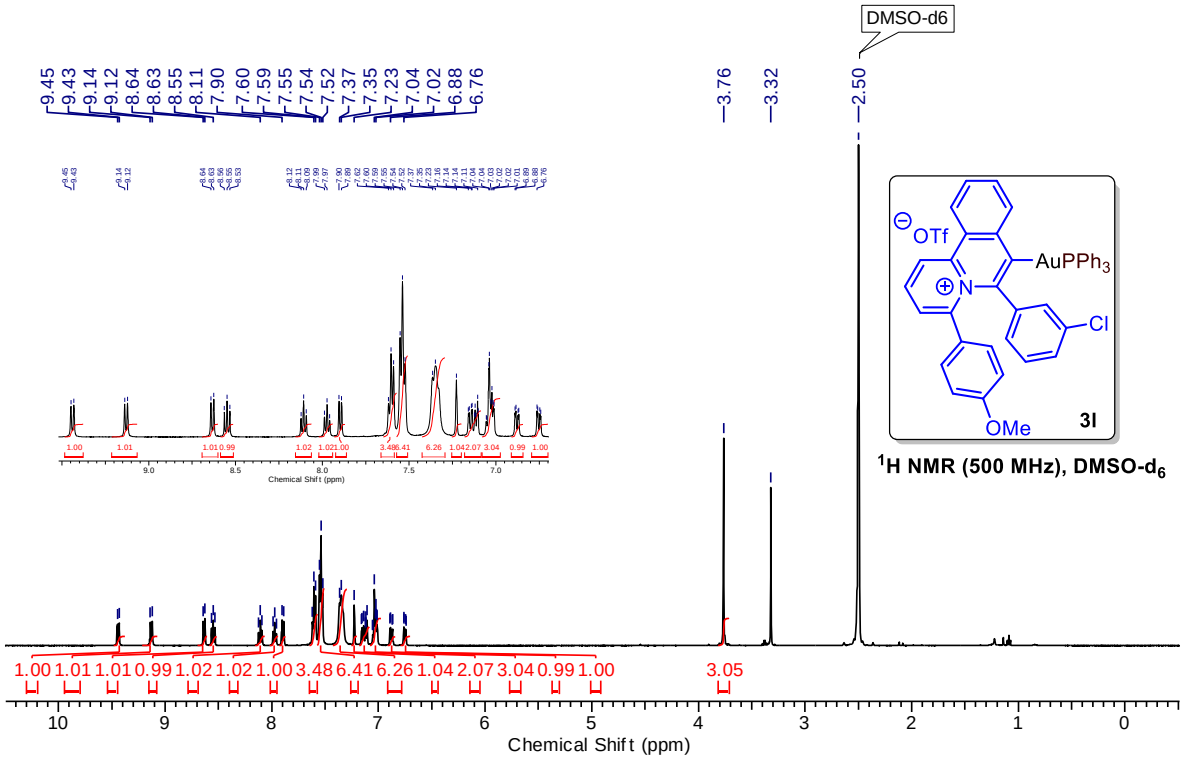
^{13}C NMR (125 MHz), DMSO-d_6


DMSO-d6
9.41 9.40 9.11 9.10 8.64 8.62 8.52 8.51 7.93 7.84 7.83 7.61 7.54 7.03 7.02 7.00 6.99 6.76 6.74 6.72 6.71
3.73 3.34 2.50 2.11
OTf
AuPPh3
N
Me
OMe
3j
1H NMR (700 MHz), DMSO-d6
1.00 1.00 0.99 0.97 1.00 1.03 1.04 4.01 6.04 5.10 1.97 1.91 1.95 1.95
3.05
3.00
Chemical Shift (ppm)

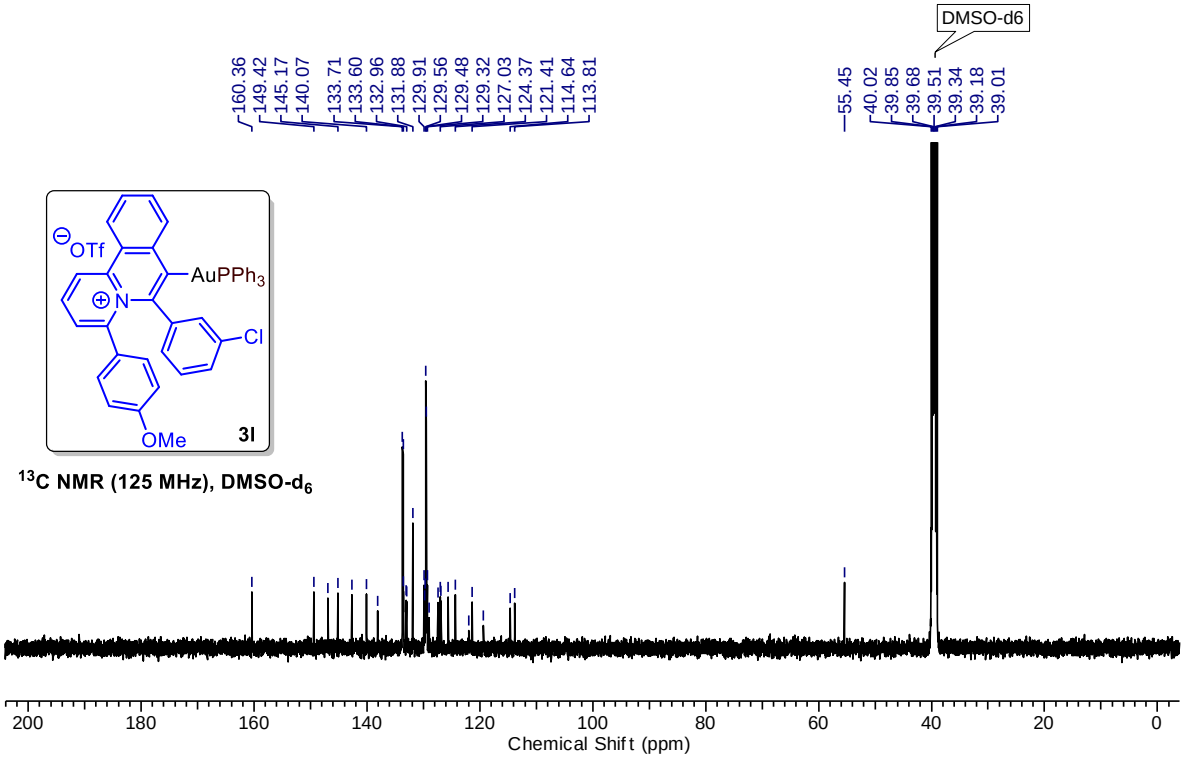

DMSO-d6
160.07 149.69 146.77 144.65 140.72 133.78 133.50 132.88 131.88 129.55 129.26 128.58 128.48 127.30 125.53 121.15 113.93
55.45 39.86 39.75 39.63 39.51 39.39 39.27 39.15 20.81
OTf
AuPPh3
N
Me
OMe
3j
13C NMR (175 MHz), DMSO-d6
Chemical Shift (ppm)


DMSO-d6
9.43 9.41 9.13 9.11 8.63 8.62 8.53 8.10 7.86 7.60 7.53 7.52 7.51 7.35 7.33 7.32 7.10 7.08 6.81 6.79 6.31 6.24 6.24
3.73 3.40 3.32 2.50
OTf
AuPPh3
N
OMe
OMe
OMe
3k
1H NMR (500 MHz), DMSO-d6
1.00 1.00 1.00 1.03 1.06 1.05 1.04 3.20 6.17 6.13 2.02 2.04 2.00 1.03
3.02 6.04
Chemical Shift (ppm)

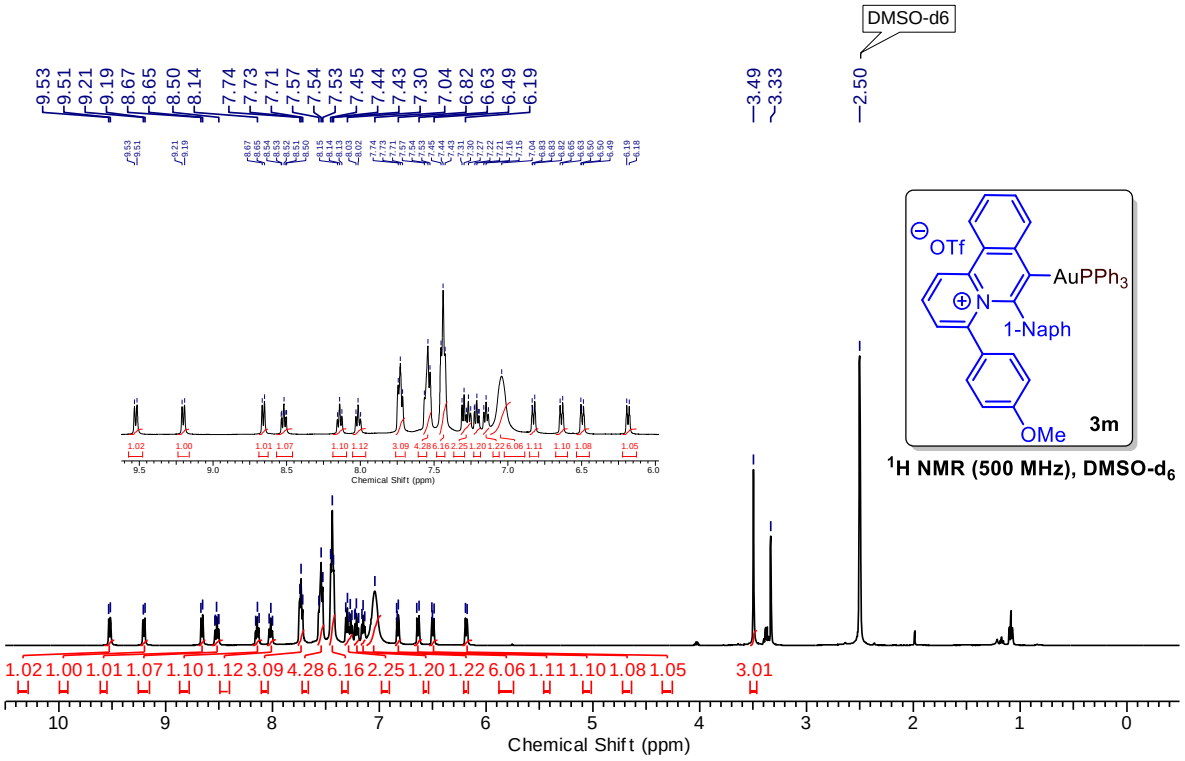

DMSO-d6
160.25 159.98 149.81 146.74 144.20 140.23 133.70 133.59 132.87 131.85 130.09 129.77 129.54 129.45 129.12 125.52 121.22 113.99 107.13 100.00
55.34 54.89 40.01 39.84 39.68 39.51 39.34 39.18 39.01
OTf
AuPPh3
N
OMe
OMe
OMe
3k
13C NMR (125 MHz), DMSO-d6
Chemical Shift (ppm)

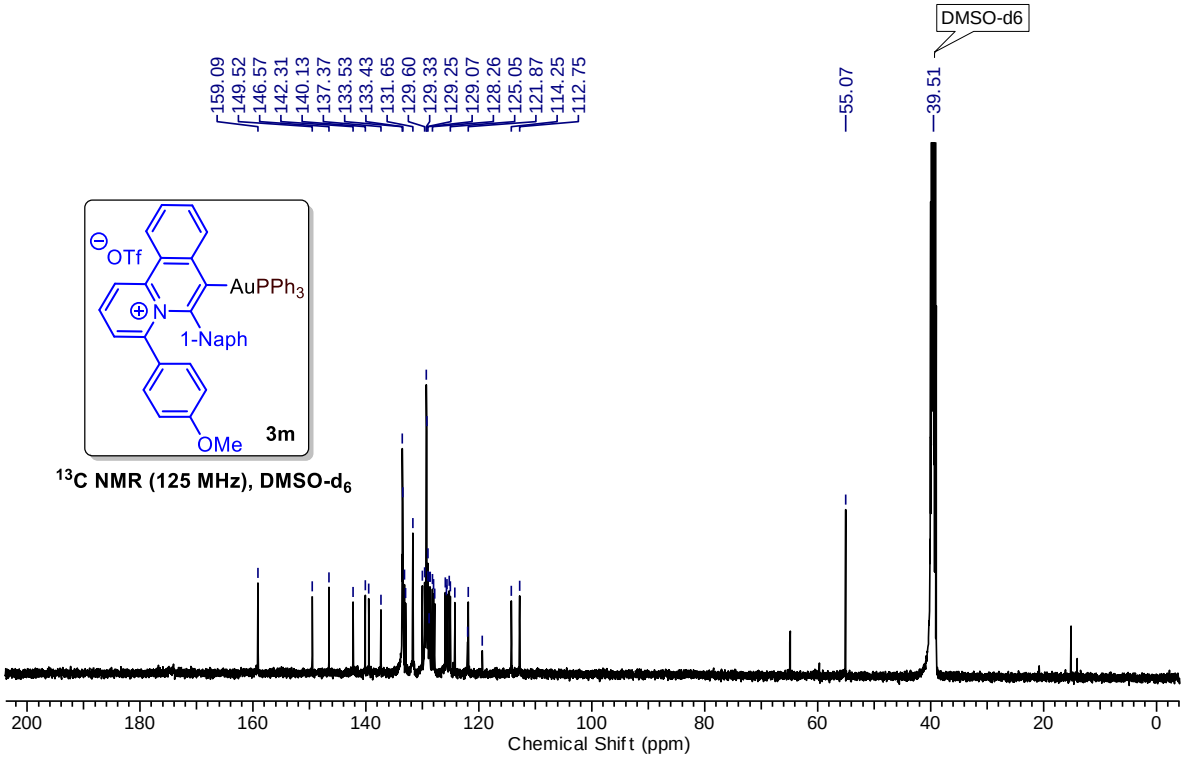


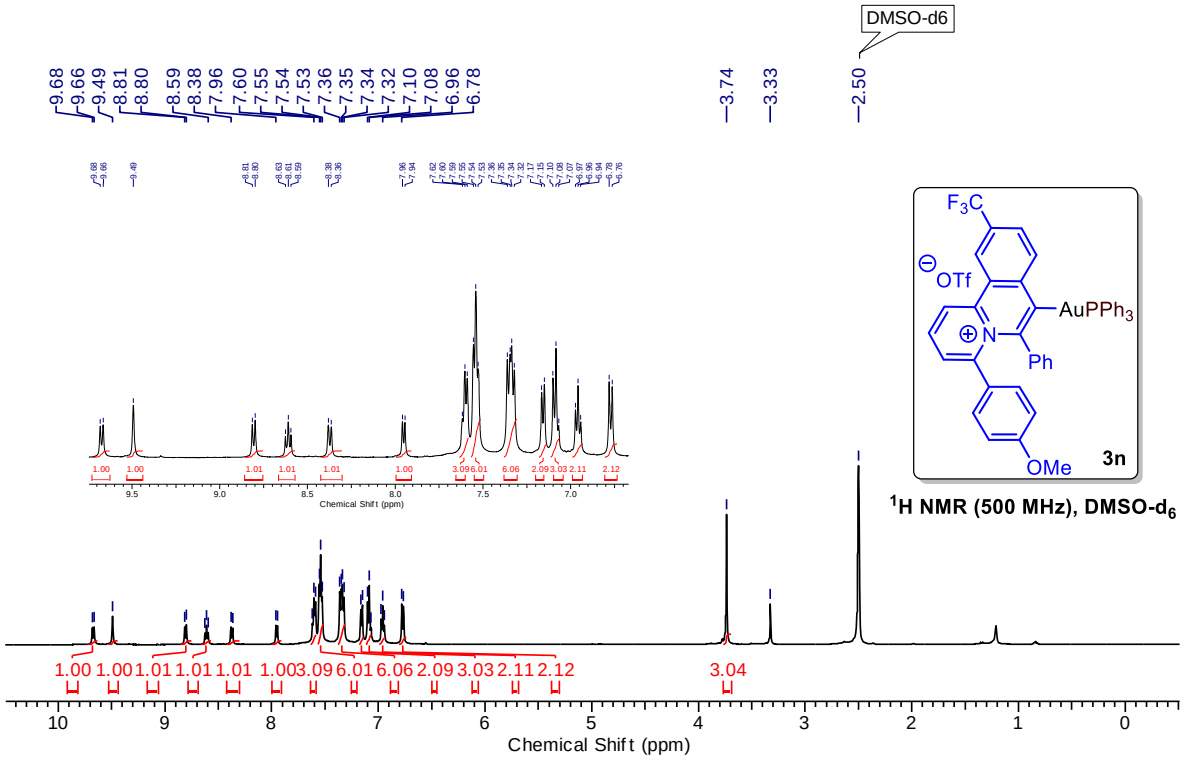
^{1}H NMR (500 MHz), DMSO-d_6

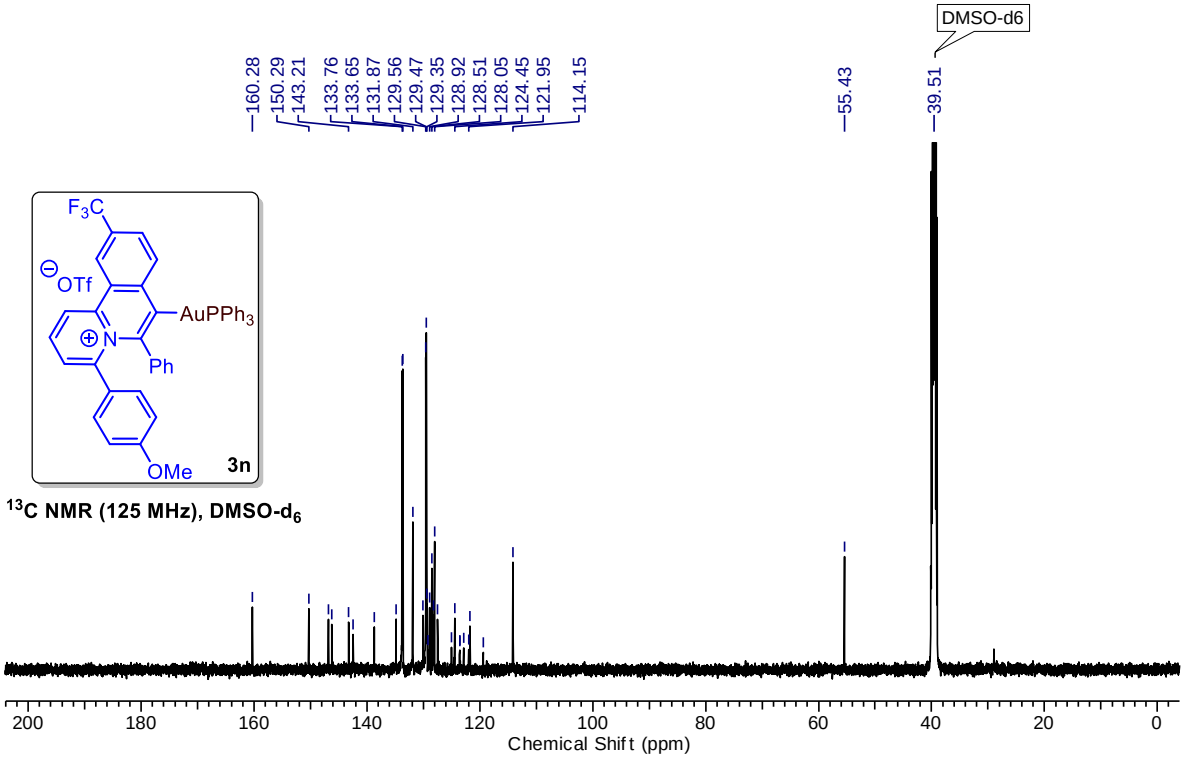


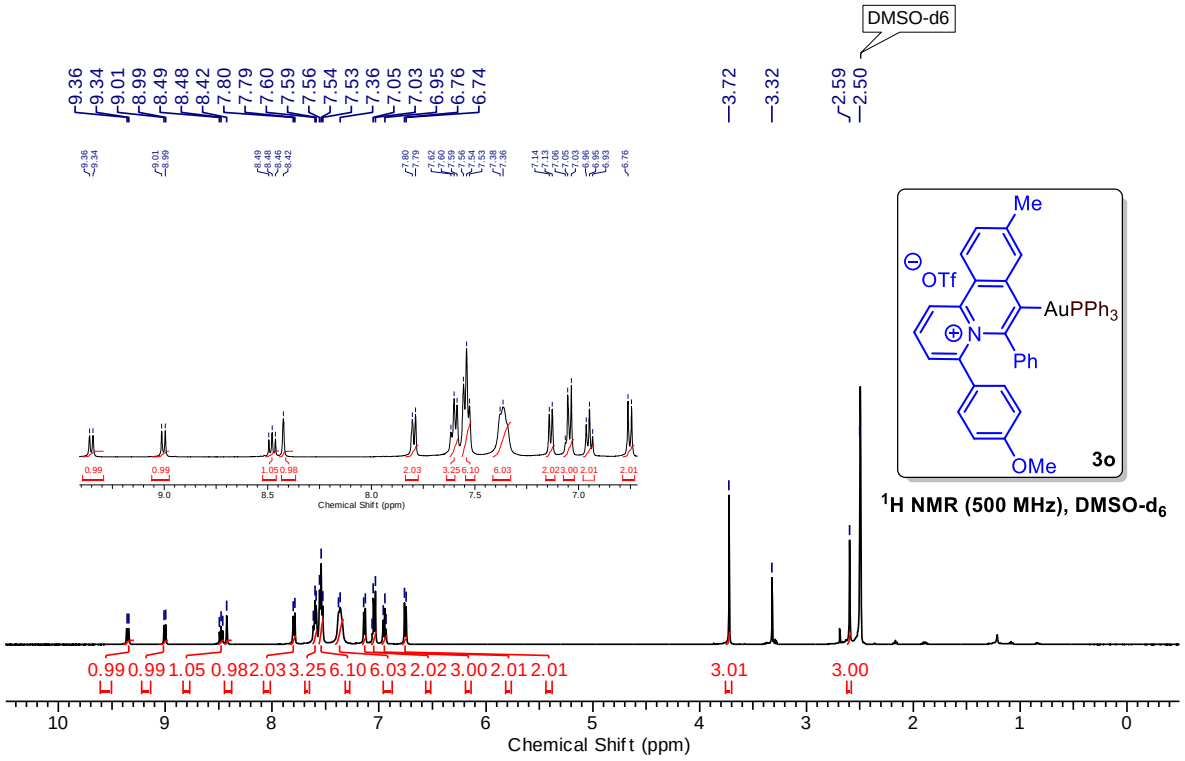
^{13}C NMR (125 MHz), DMSO-d_6


DMSO-d6
9.53
9.51
9.21
9.19
8.67
8.65
8.50
8.14
7.74
7.73
7.71
7.57
7.54
7.53
7.45
7.44
7.43
7.30
7.04
6.82
6.63
6.49
6.19
3.49
3.33
2.50
OTf
AuPPh3
N
1-Naph
OMe
3m
1H NMR (500 MHz), DMSO-d6
1.02 1.00 1.01 1.07 1.10 1.12 3.09 4.28 6.16 2.25 1.20 1.22 6.06 1.11 1.10 1.08 1.05
3.01
Chemical Shift (ppm)

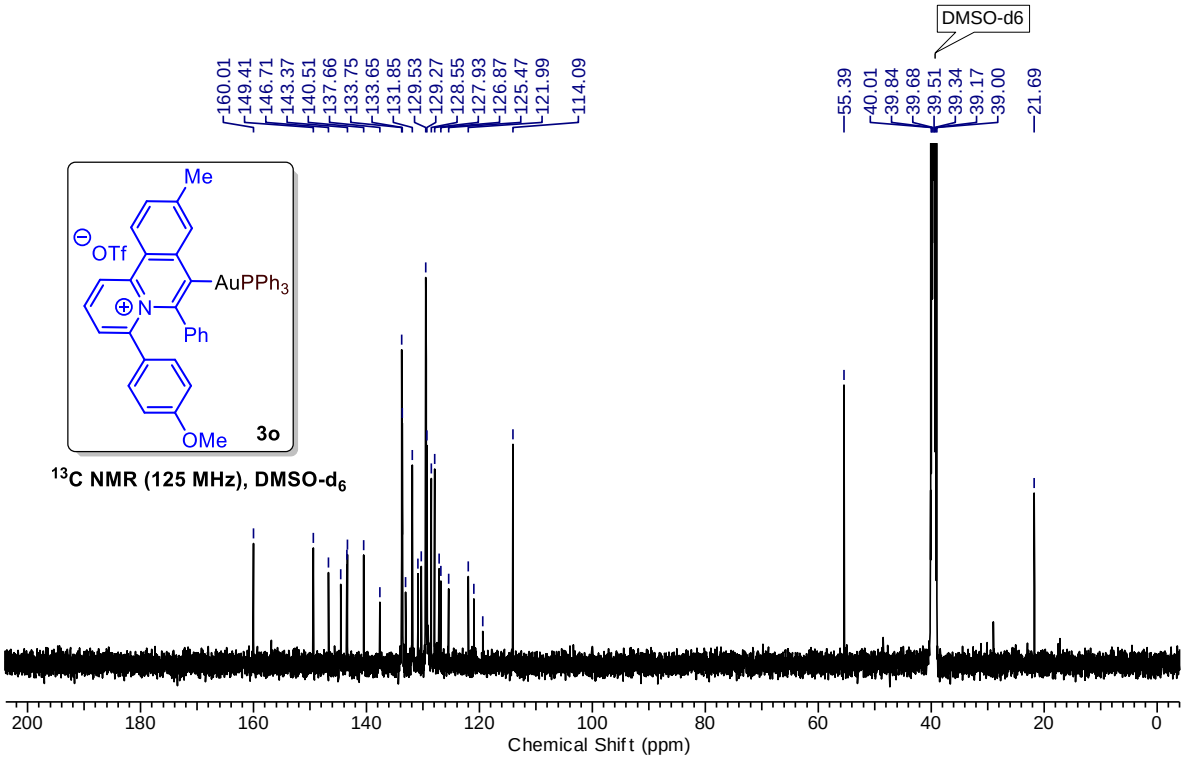

DMSO-d6
159.09
149.52
146.57
142.31
140.13
137.37
133.53
133.43
131.65
129.60
129.33
129.25
129.07
128.26
125.05
121.87
114.25
112.75
55.07
39.51
OTf
AuPPh3
N
1-Naph
OMe
3m
13C NMR (125 MHz), DMSO-d6
Chemical Shift (ppm)


DMSO-d6
9.68
9.66
9.49
8.81
8.80
8.59
8.38
7.96
7.60
7.55
7.54
7.53
7.36
7.35
7.34
7.32
7.10
7.08
6.96
6.78
3.74
3.33
2.50
F3C
OTf
AuPPh3
N
Ph
OMe
3n
1H NMR (500 MHz), DMSO-d6
1.00 1.00 1.01 1.01 1.01 1.00 3.09 6.01 6.06 2.09 3.03 2.11 2.12
3.04
Chemical Shift (ppm)

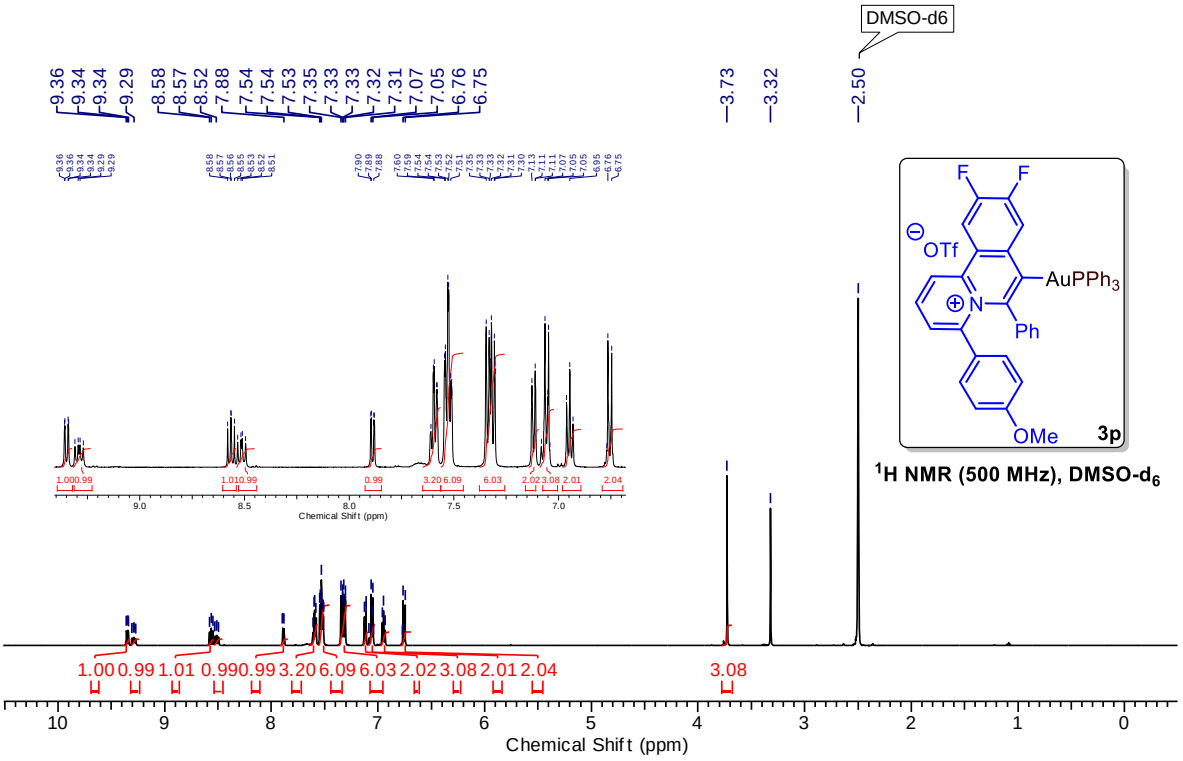

DMSO-d6
160.28
150.29
143.21
133.76
133.65
131.87
129.56
129.47
129.35
128.92
128.51
128.05
124.45
121.95
114.15
55.43
39.51
F3C
OTf
AuPPh3
N
Ph
OMe
3n
13C NMR (125 MHz), DMSO-d6
Chemical Shift (ppm)

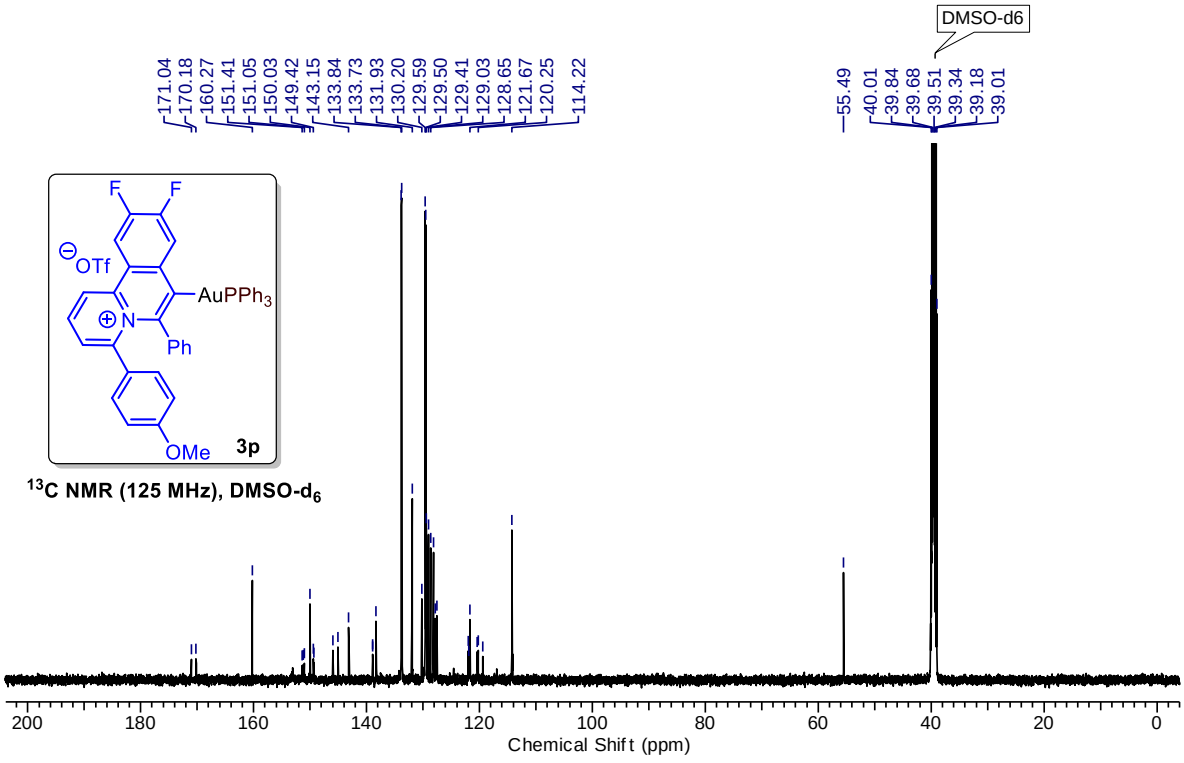


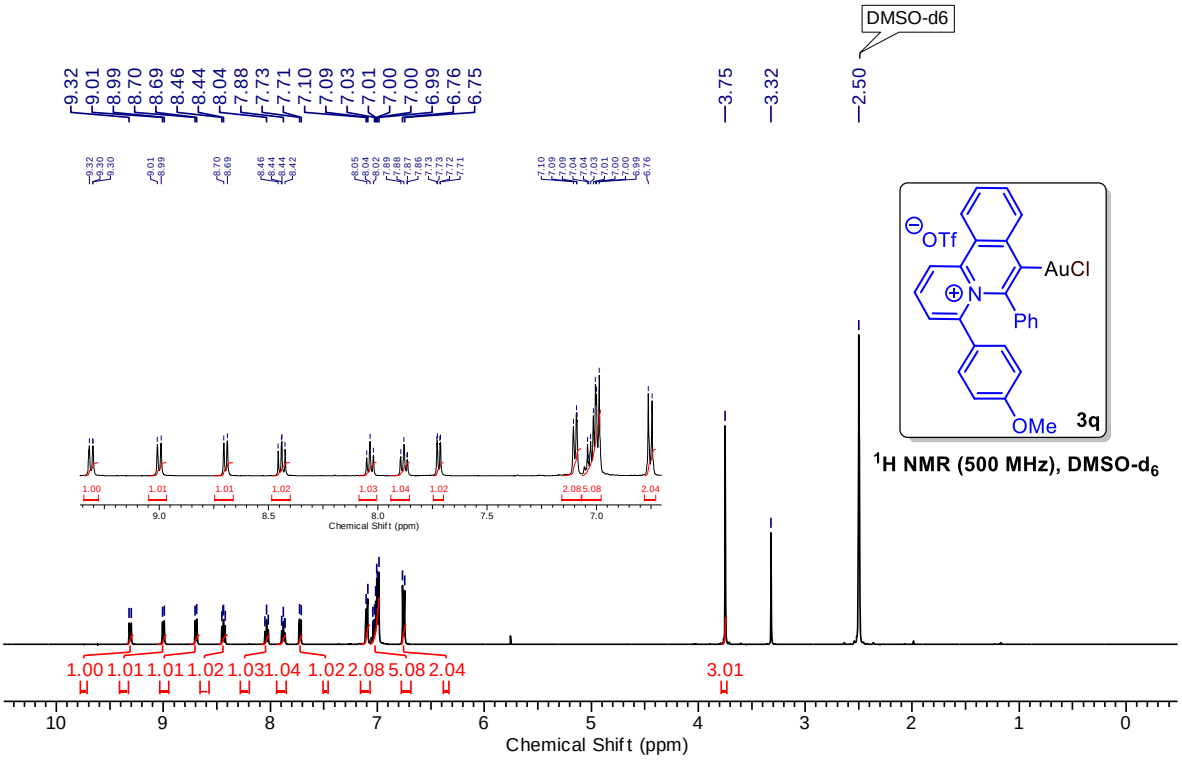
^{1}H NMR (500 MHz), DMSO-d_6

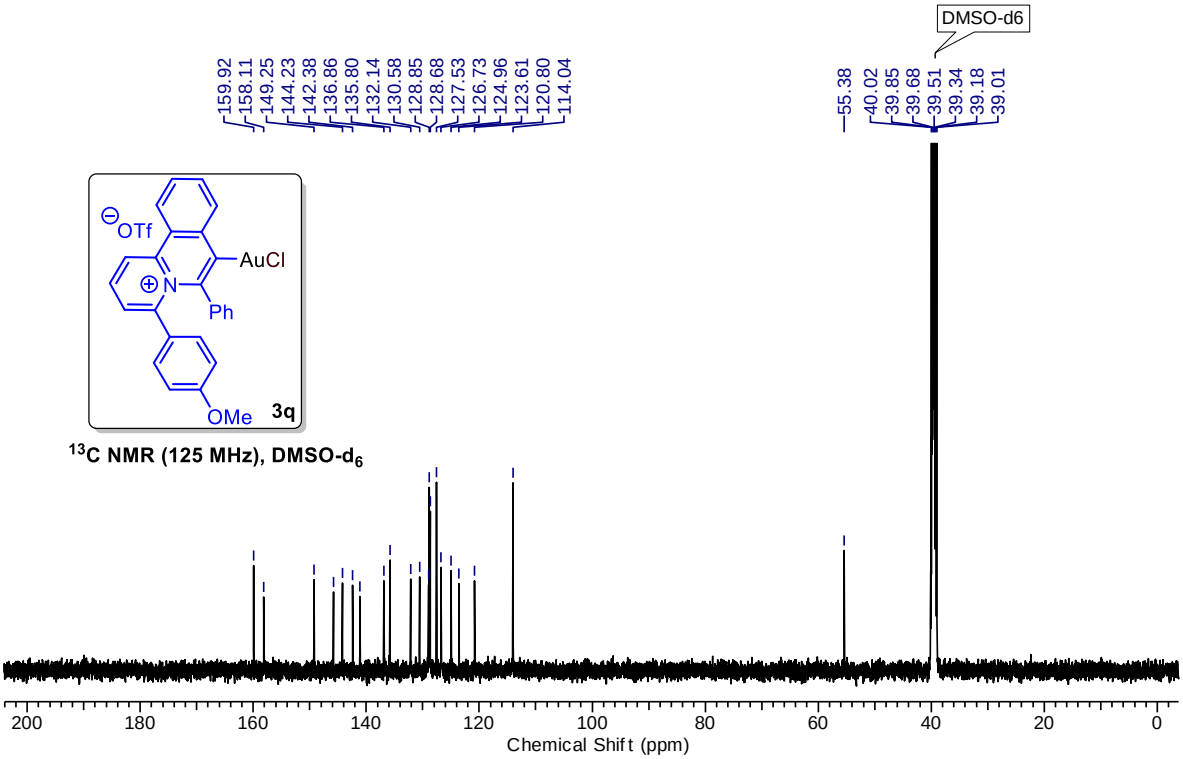


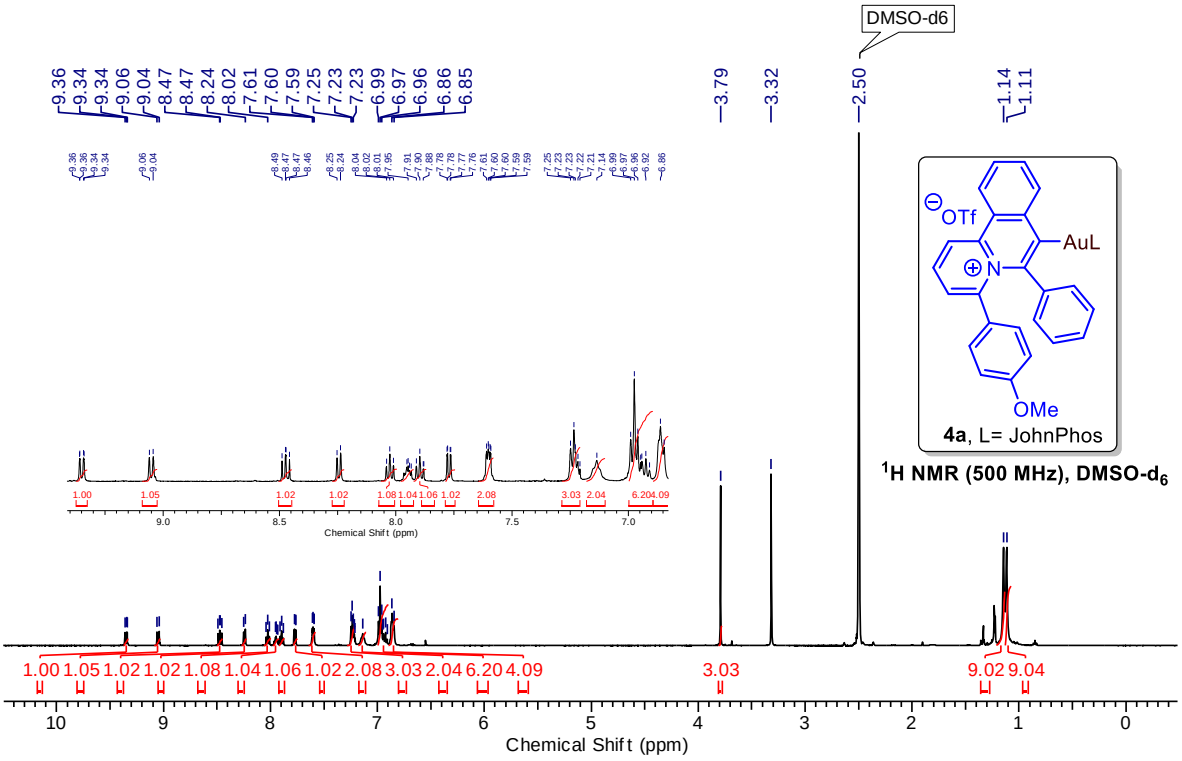
^{13}C NMR (125 MHz), DMSO-d_6

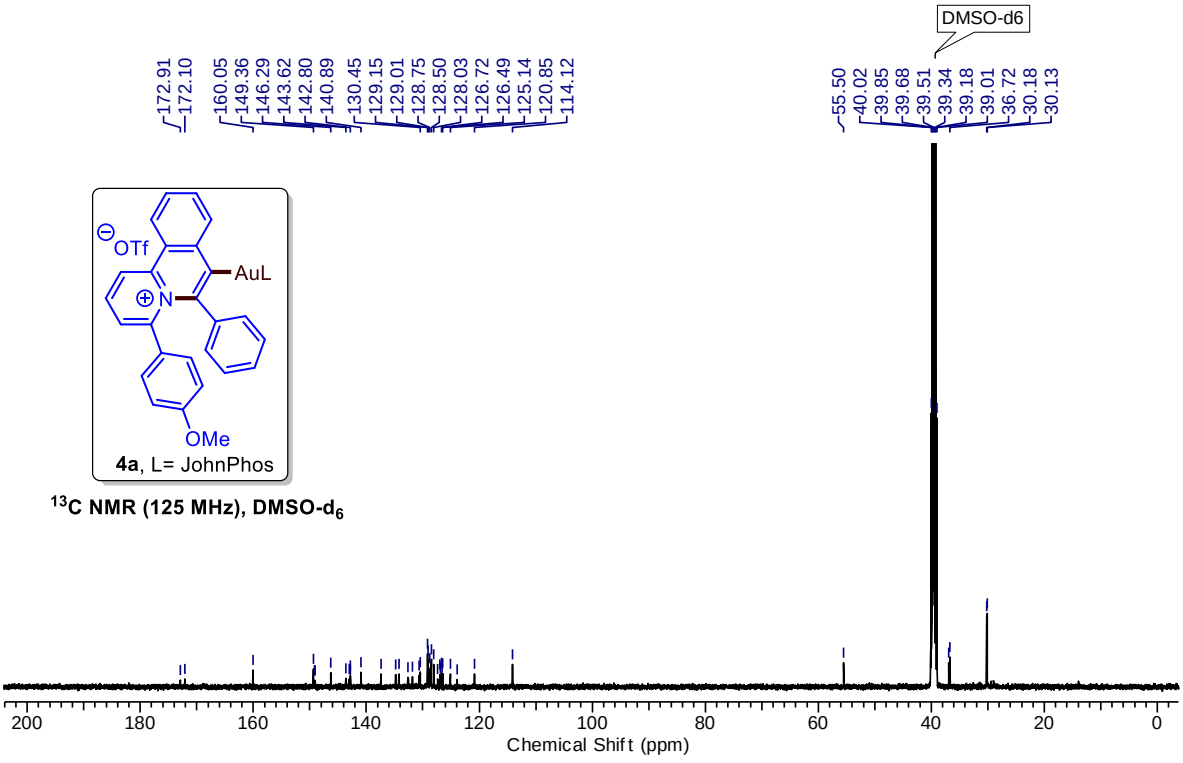

DMSO-d6
9.36
9.34
9.34
9.29
8.58
8.57
8.52
7.88
7.54
7.54
7.53
7.35
7.33
7.33
7.32
7.31
7.07
7.05
6.76
6.75
3.73
3.32
2.50
F
F
OTf
AuPPh3
N
Ph
OMe
3p
1H NMR (500 MHz), DMSO-d6
1.00 0.99 1.01 0.99 0.99 3.20 6.09 6.03 2.02 3.08 2.01 2.04
3.08
Chemical Shift (ppm)

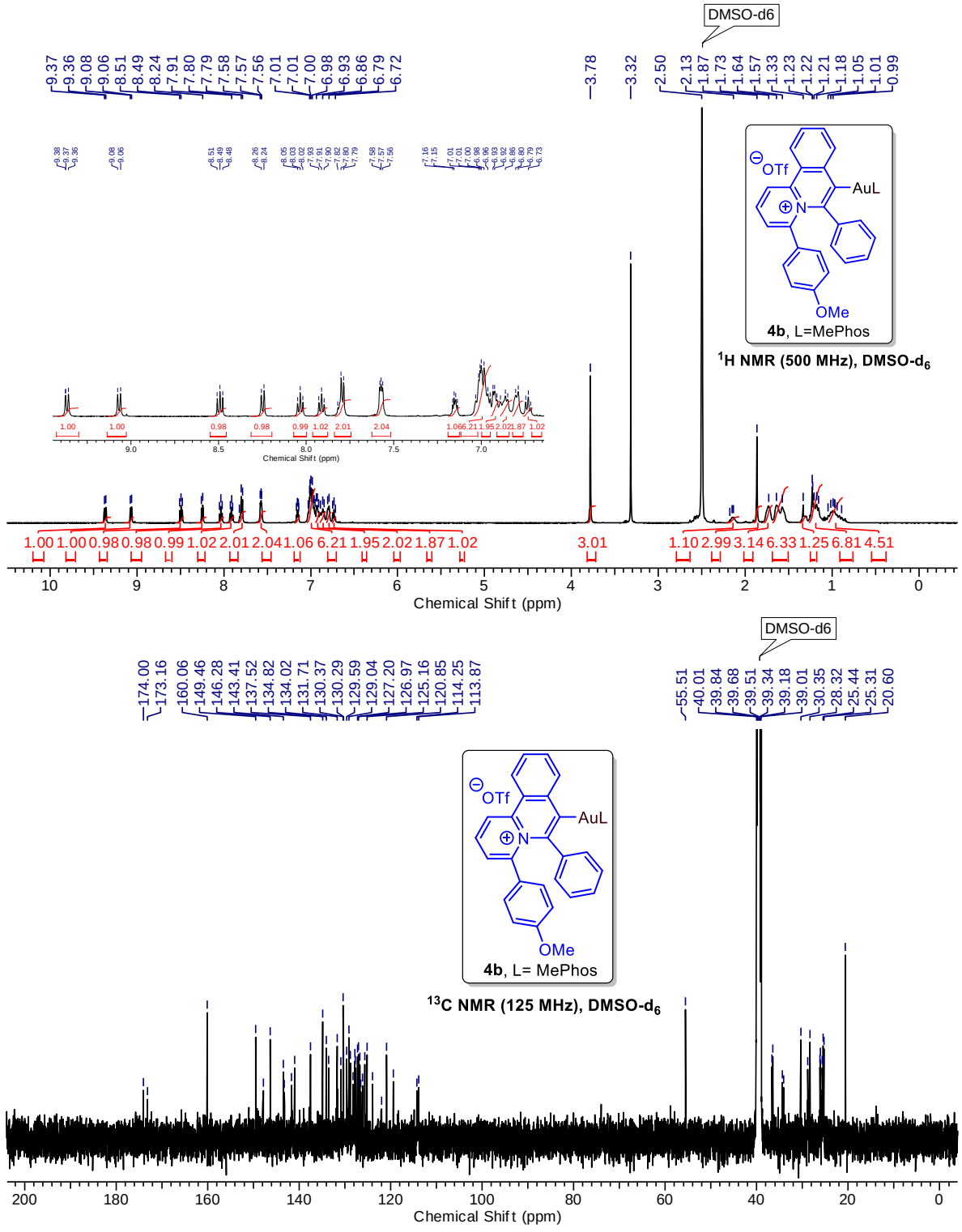

DMSO-d6
171.04
170.18
160.27
151.41
151.05
150.03
149.42
143.15
133.84
133.73
131.93
130.20
129.59
129.50
129.41
129.03
128.65
121.67
120.25
114.22
55.49
40.01
39.84
39.68
39.51
39.34
39.18
39.01
F
F
OTf
AuPPh3
N
Ph
OMe
3p
13C NMR (125 MHz), DMSO-d6
Chemical Shift (ppm)

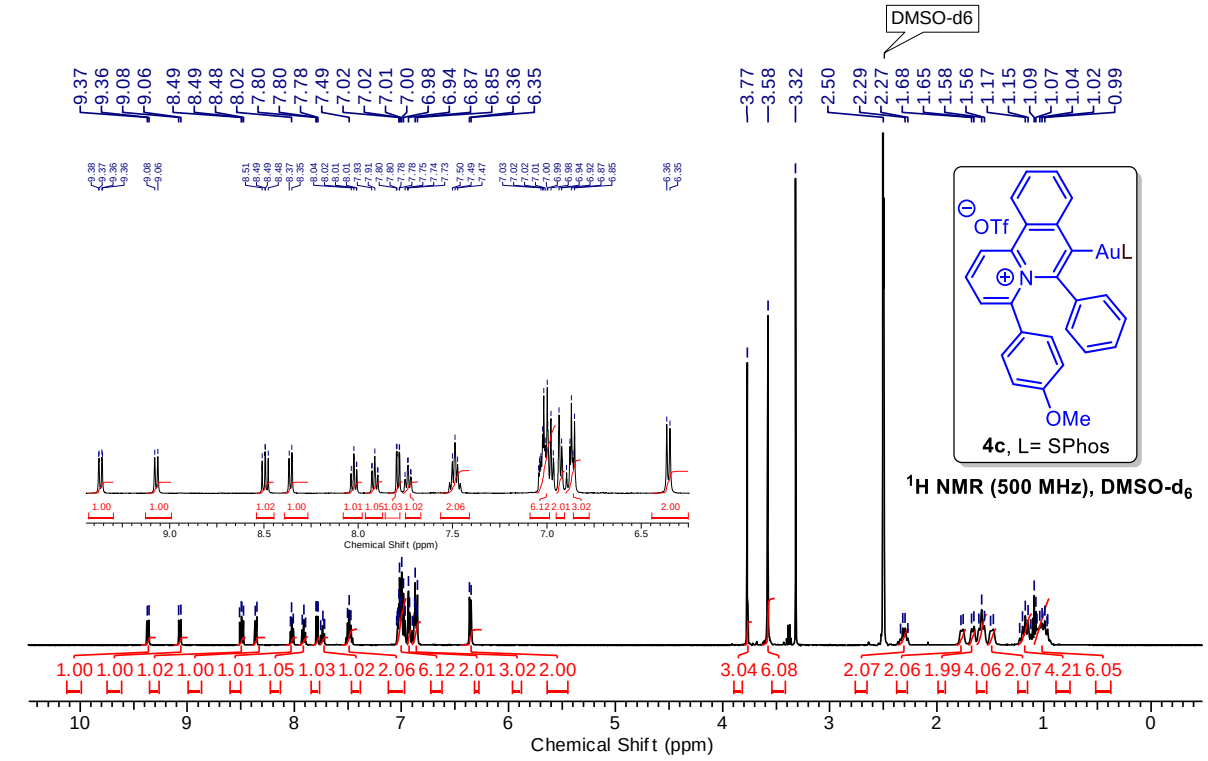

DMSO-d6
9.32
9.01
8.99
8.70
8.69
8.46
8.44
8.04
7.88
7.73
7.71
7.10
7.09
7.03
7.01
7.00
7.00
6.99
6.76
6.75
3.75
3.32
2.50
OTf
AuCl
N
Ph
OMe
3q
1H NMR (500 MHz), DMSO-d6
1.00 1.01 1.01 1.02 1.03 1.04 1.02 2.08 5.08 2.04
3.01
Chemical Shift (ppm)

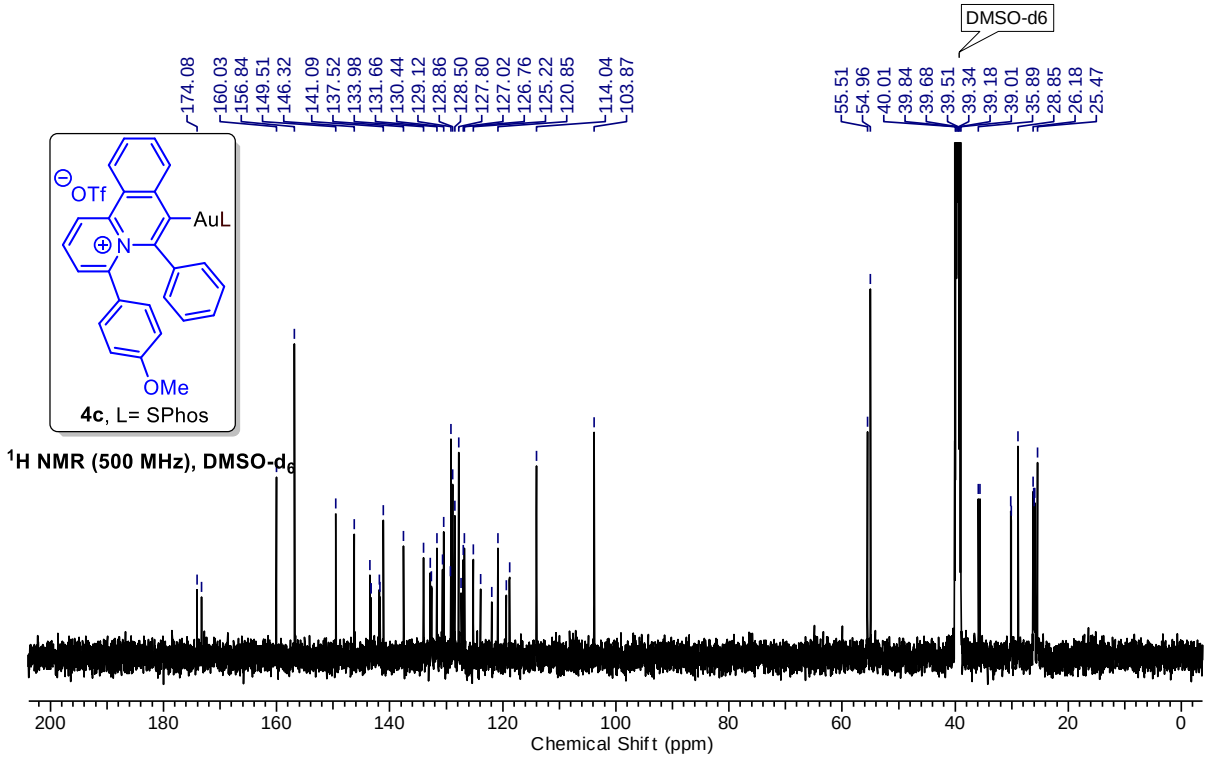

DMSO-d6
159.92
158.11
149.25
144.23
142.38
136.86
135.80
132.14
130.58
128.85
128.68
127.53
126.73
124.96
123.61
120.80
114.04
55.38
40.02
39.85
39.68
39.51
39.34
39.18
39.01
OTf
AuCl
N
Ph
OMe
3q
13C NMR (125 MHz), DMSO-d6
Chemical Shift (ppm)

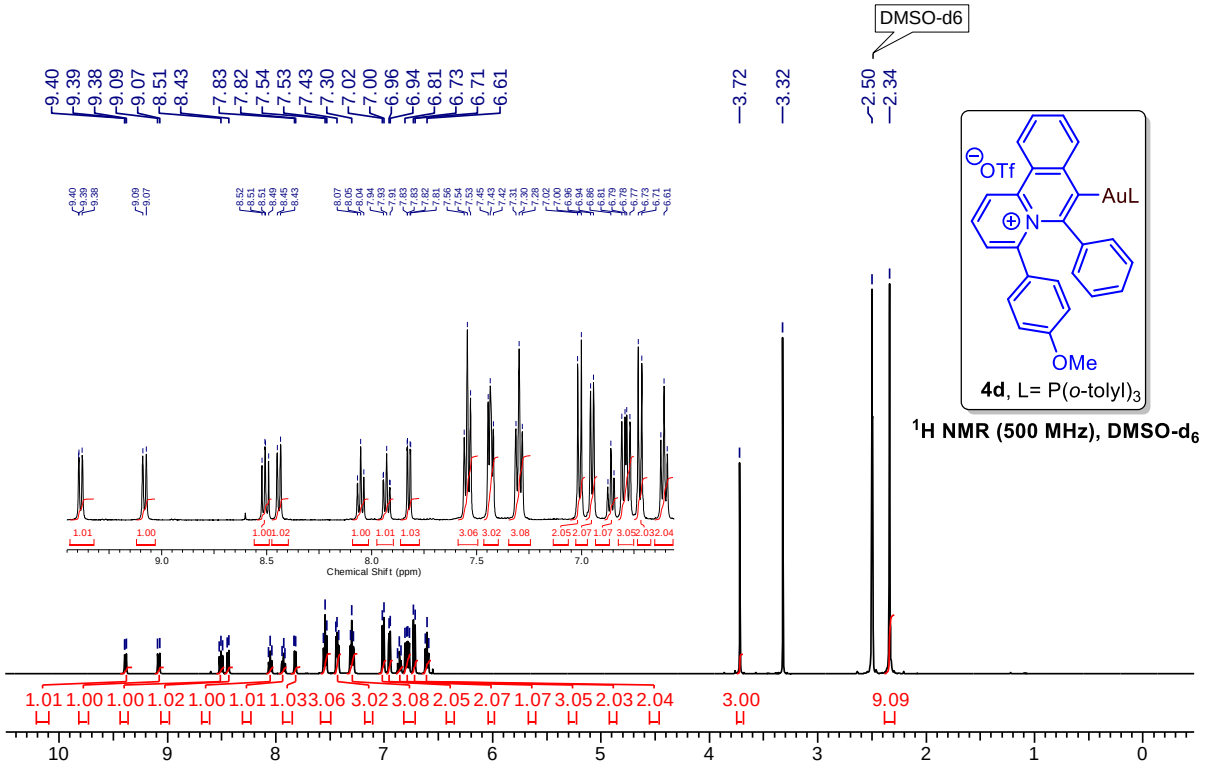

DMSO-d6
9.36 9.34 9.34 9.06 9.04 8.47 8.47 8.24 8.02 7.61 7.60 7.59 7.25 7.23 7.23 6.99 6.97 6.96 6.86 6.85
3.79 3.32 2.50 1.14 1.11
OTf
AuL
N
OMe
4a, L= JohnPhos
1H NMR (500 MHz), DMSO-d6
1.00 1.05 1.02 1.02 1.08 1.04 1.06 1.02 2.08 3.03 2.04 6.20 4.09
3.03
9.02 9.04
Chemical Shift (ppm)

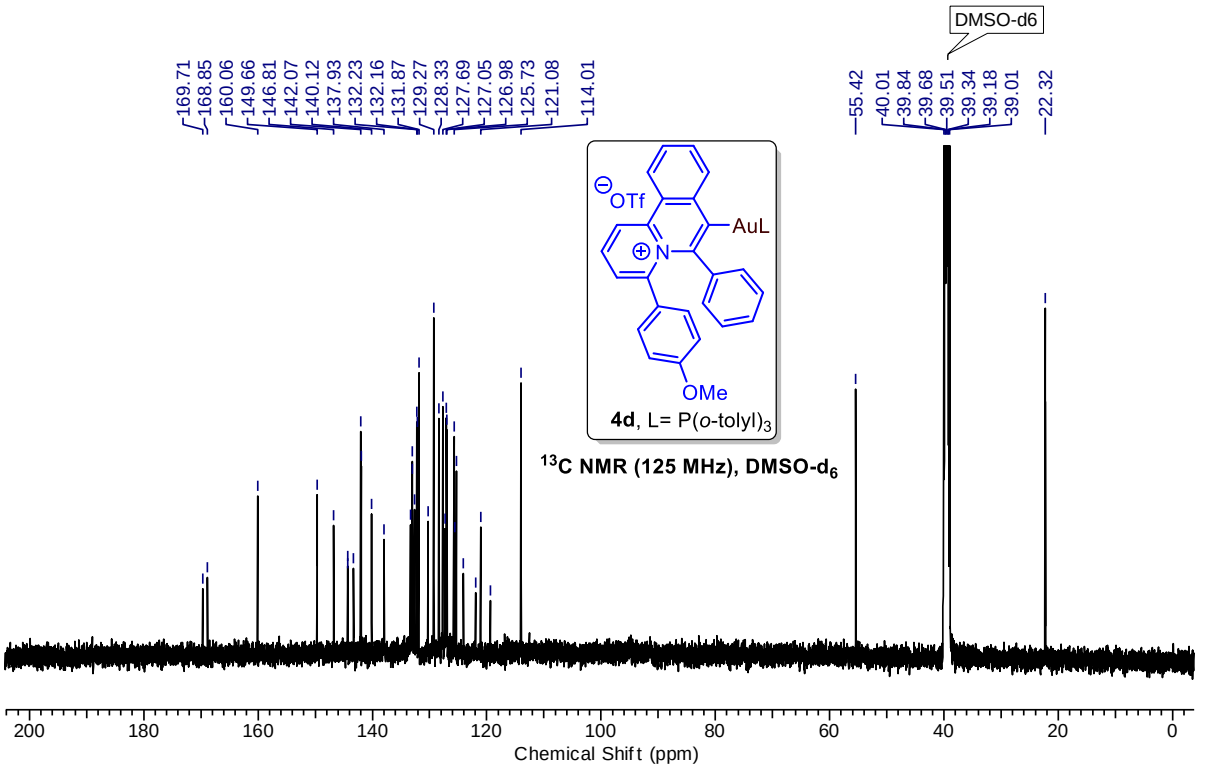

DMSO-d6
172.91 172.10 160.05 149.36 146.29 143.62 142.80 140.89 130.45 129.15 129.01 128.75 128.50 128.03 126.72 126.49 125.14 120.85 114.12
55.50 40.02 39.85 39.68 39.51 39.34 39.18 39.01 36.72 30.18 30.13
OTf
AuL
N
OMe
4a, L= JohnPhos
13C NMR (125 MHz), DMSO-d6
Chemical Shift (ppm)

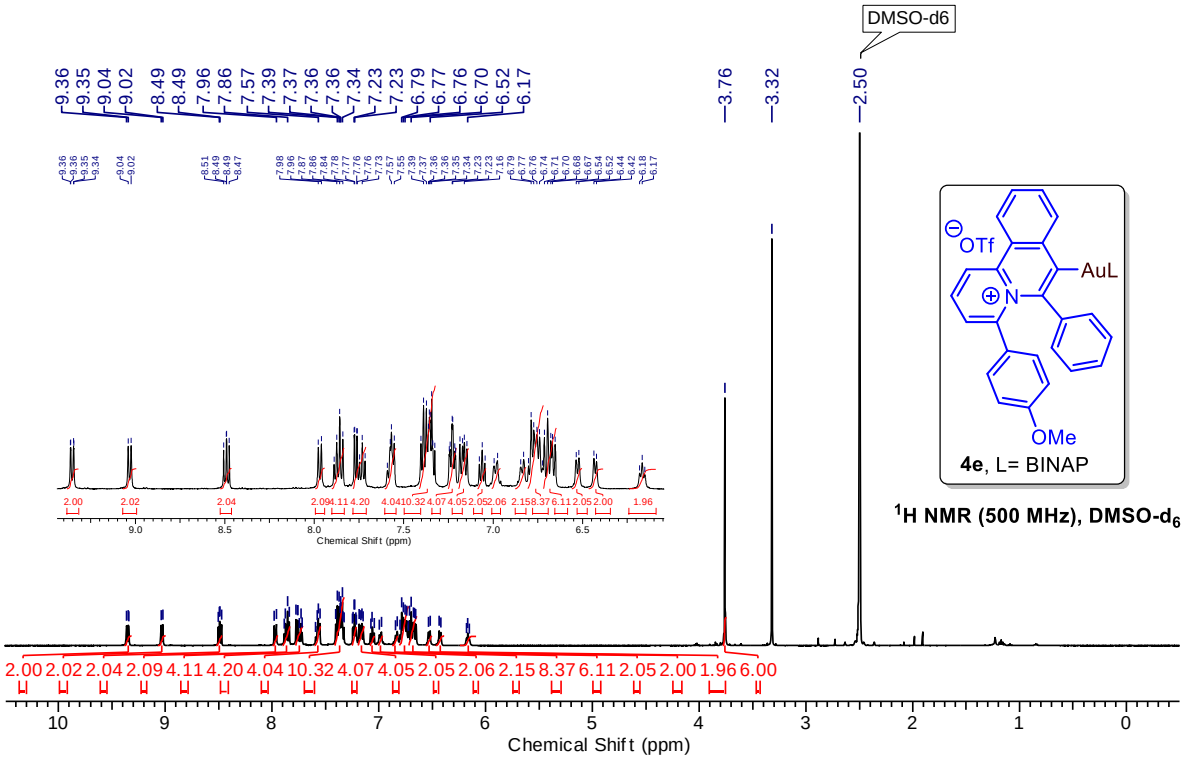

DMSO-d6
OTf
AuL
OMe
4b, L=MePhos
1H NMR (500 MHz), DMSO-d6
Chemical Shift (ppm)
DMSO-d6
OTf
AuL
OMe
4b, L= MePhos
13C NMR (125 MHz), DMSO-d6
Chemical Shift (ppm)

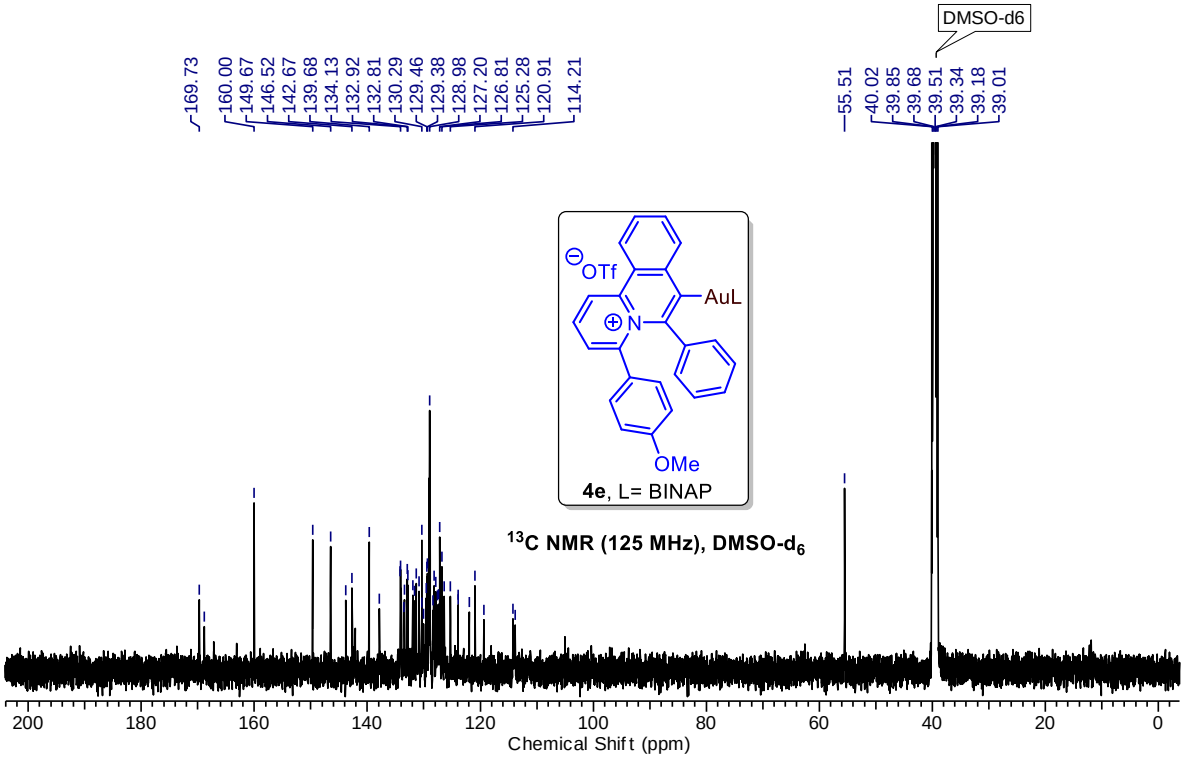

DMSO-d6
OTf
AuL
OMe
4c, L= SPhos
1H NMR (500 MHz), DMSO-d6
Chemical Shift (ppm)

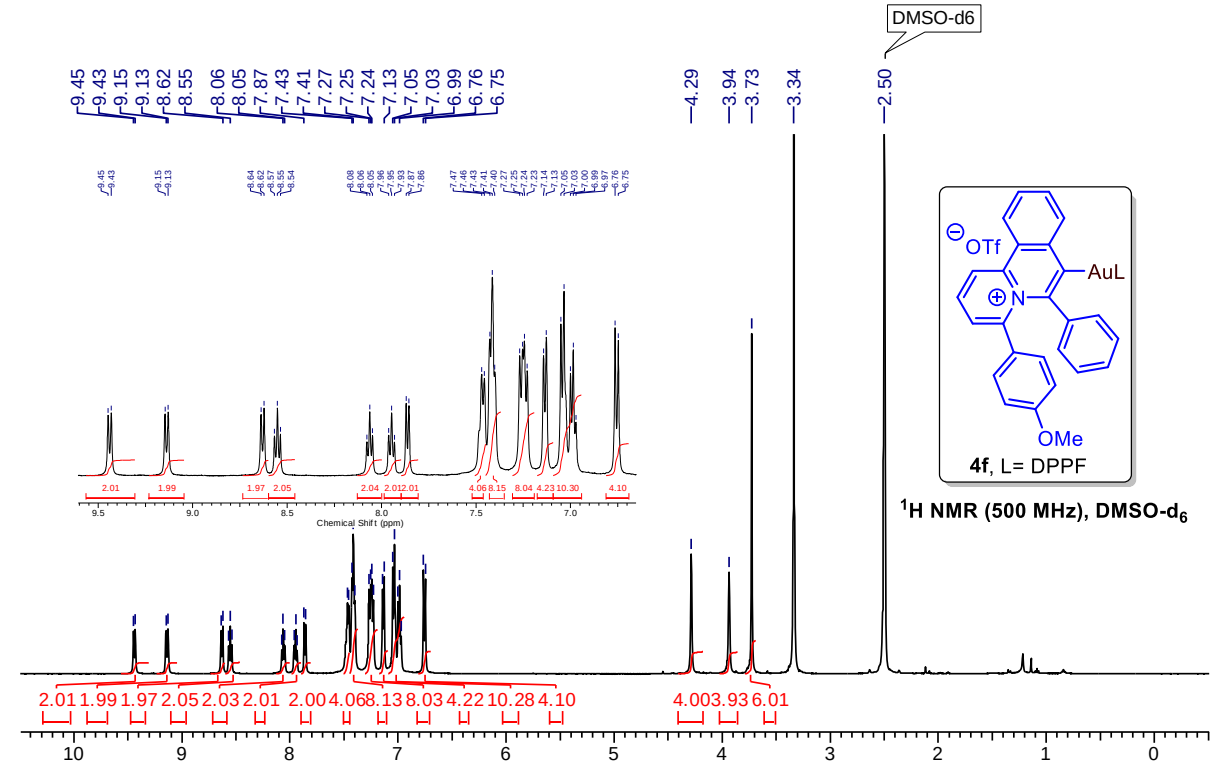

DMSO-d6
OTf
AuL
OMe
4c, L= SPhos
1H NMR (500 MHz), DMSO-d6
Chemical Shift (ppm)

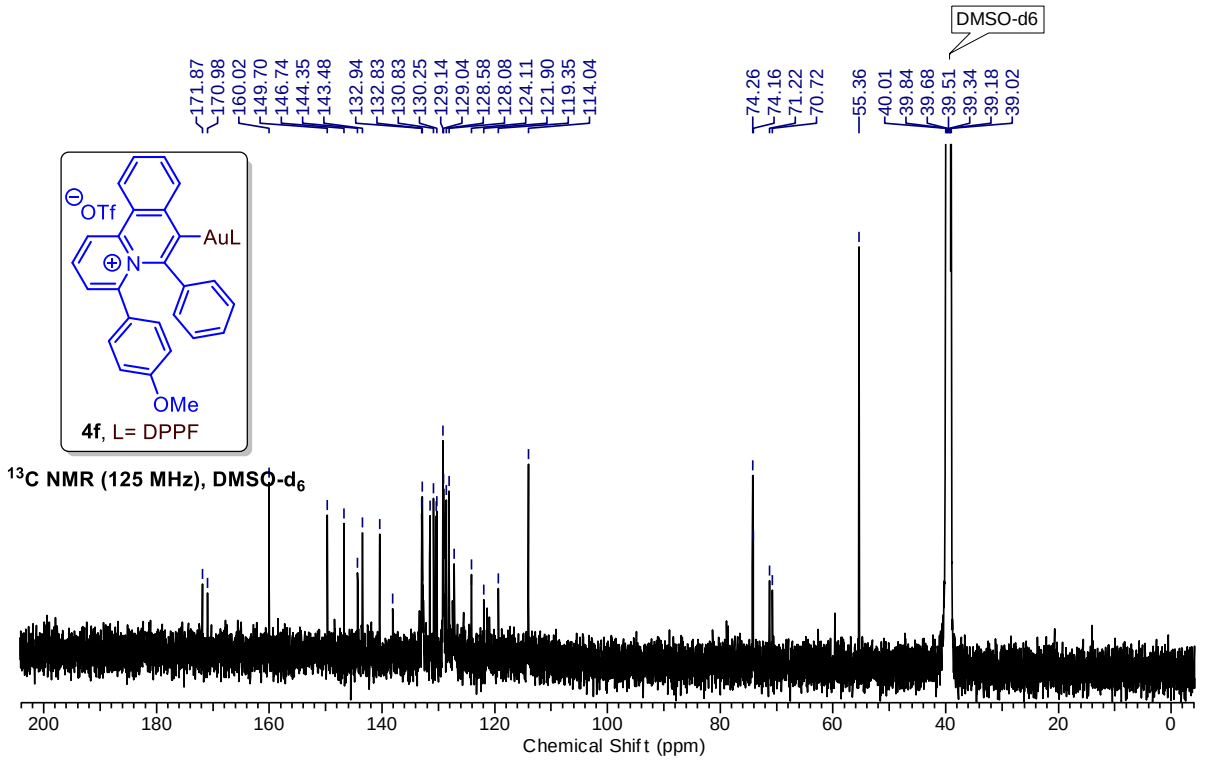

DMSO-d6
9.40 9.39 9.38 9.09 9.07 8.51 8.43 7.83 7.82 7.54 7.53 7.43 7.30 7.02 7.00 6.96 6.94 6.81 6.73 6.71 6.61
3.72 3.32 2.50 2.34
OTf
AuL
N
OMe
4d, L= P(o-tolyl)3
1H NMR (500 MHz), DMSO-d6
1.01 1.00 1.00 1.02 1.00 1.01 1.03 3.06 3.02 3.08 2.05 2.07 1.07 3.05 2.03 2.04 3.00 9.09
Chemical Shift (ppm)

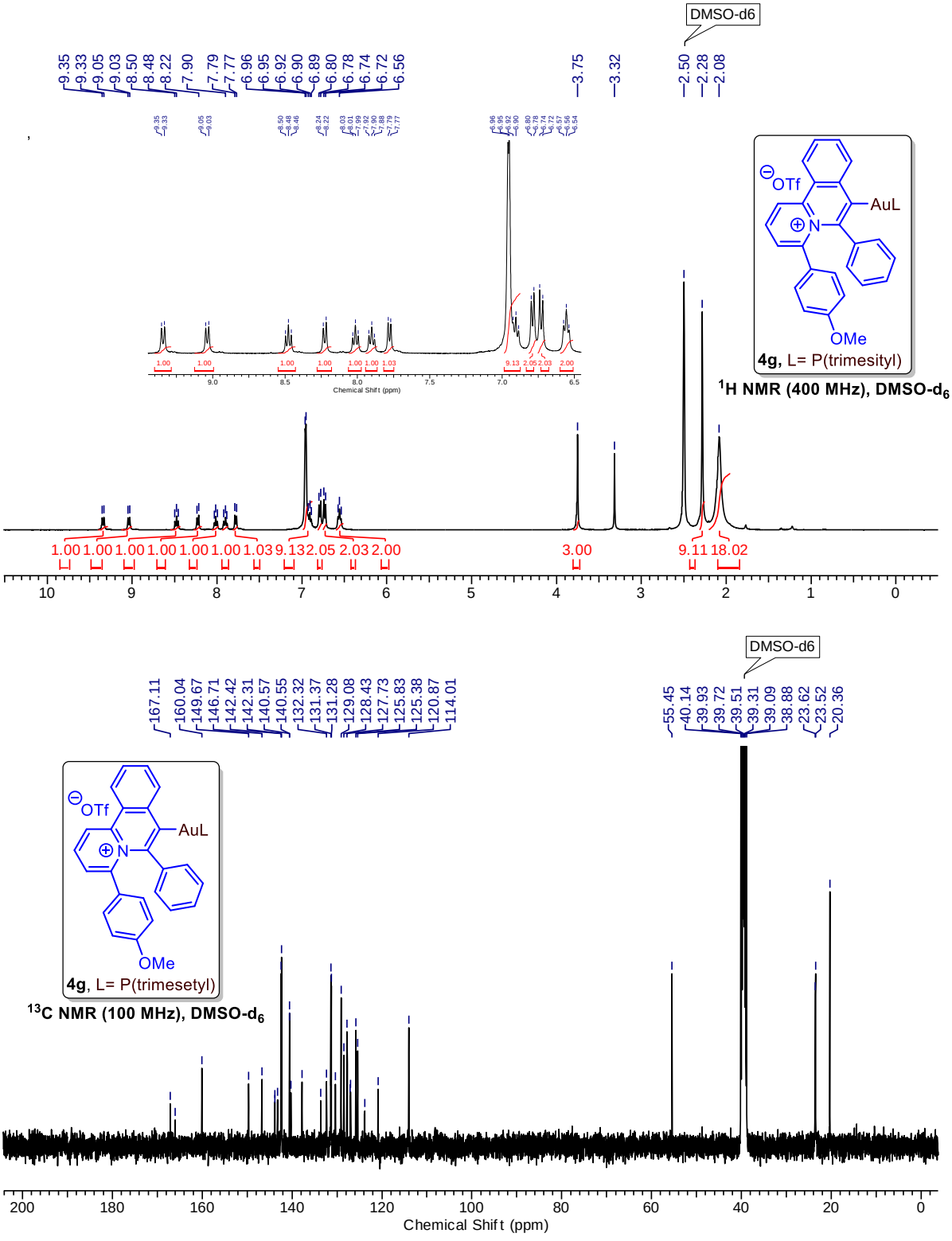

DMSO-d6
169.71 168.85 160.06 149.66 146.81 142.07 140.12 137.93 132.23 132.16 131.87 129.27 128.33 127.69 127.05 126.98 125.73 121.08 114.01
55.42 40.01 39.84 39.68 39.51 39.34 39.18 39.01 22.32
OTf
AuL
N
OMe
4d, L= P(o-tolyl)3
13C NMR (125 MHz), DMSO-d6
Chemical Shift (ppm)

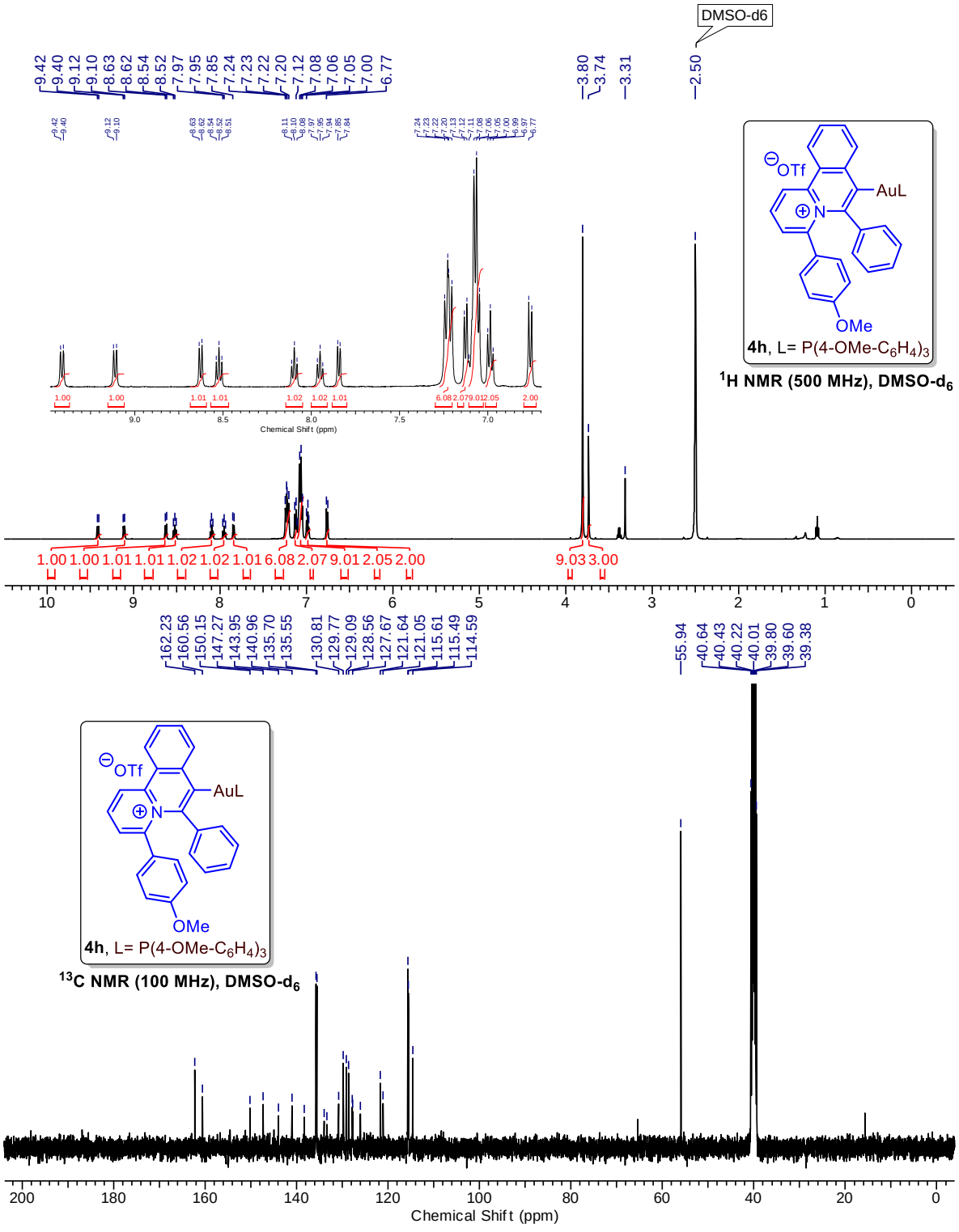

DMSO-d6
9.36 9.35 9.04 9.02 8.49 8.49 7.96 7.86 7.57 7.39 7.37 7.36 7.36 7.34 7.23 7.23 6.79 6.77 6.76 6.70 6.52 6.17
3.76
3.32
2.50
OTf
AuL
N
OMe
4e, L= BINAP
1H NMR (500 MHz), DMSO-d6
2.00 2.02 2.04 2.09 4.11 4.20 4.04 10.32 4.07 4.05 2.05 2.06 2.15 8.37 6.11 2.05 2.00 1.96 6.00
Chemical Shift (ppm)

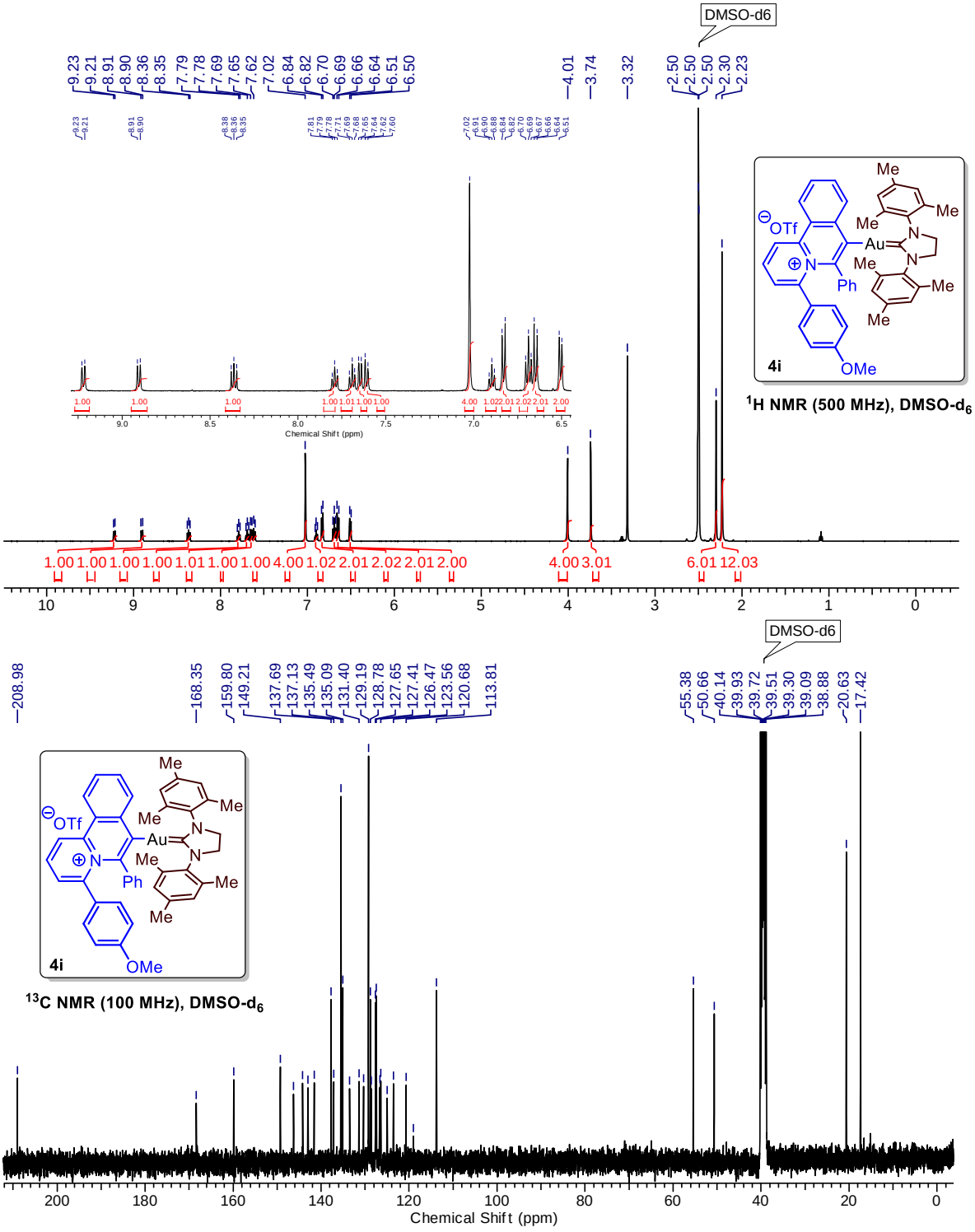

DMSO-d6
169.73 160.00 149.67 146.52 142.67 139.68 134.13 132.92 132.81 130.29 129.46 129.38 128.98 127.20 126.81 125.28 120.91 114.21
55.51 40.02 39.85 39.68 39.51 39.34 39.18 39.01
OTf
AuL
N
OMe
4e, L= BINAP
13C NMR (125 MHz), DMSO-d6
Chemical Shift (ppm)

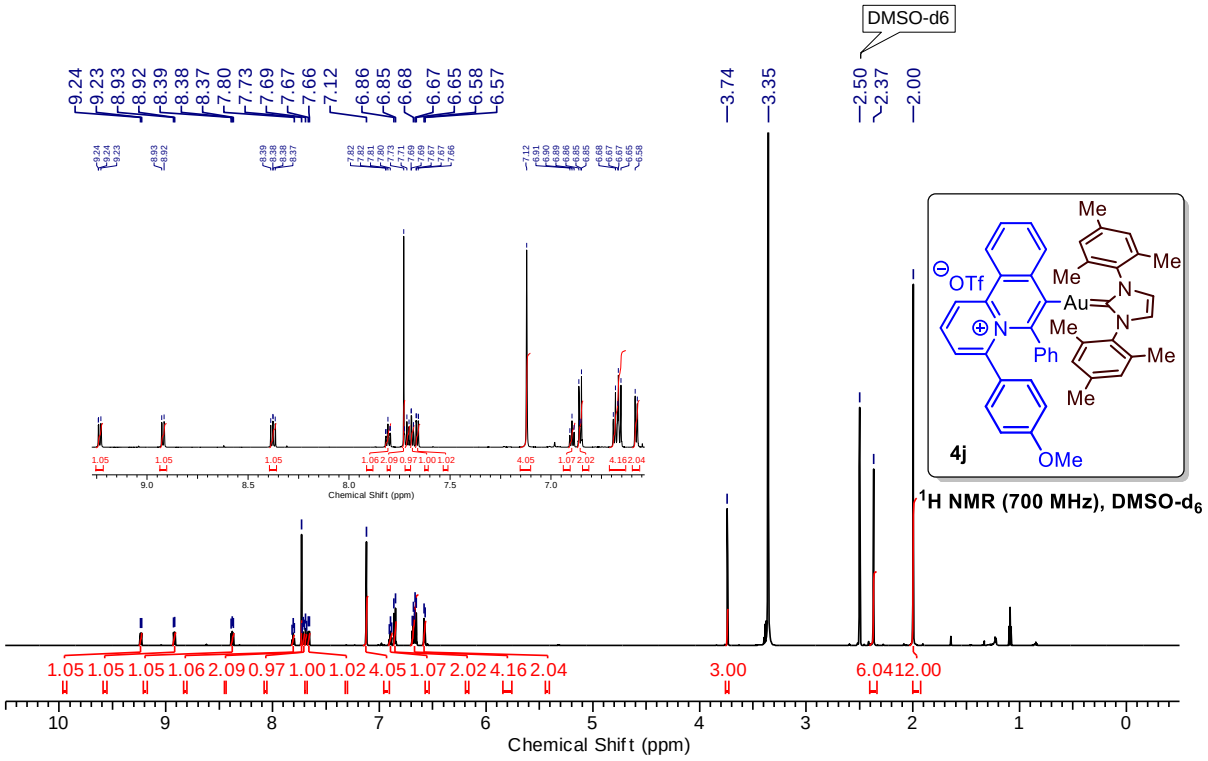

DMSO-d6
9.45 9.43 9.15 9.13 8.62 8.55 8.06 8.05 7.87 7.43 7.41 7.27 7.25 7.24 7.13 7.05 7.03 6.99 6.76 6.75
4.29 3.94 3.73 3.34 2.50
OTf
AuL
N
OMe
4f, L= DPPF
1H NMR (500 MHz), DMSO-d6
2.01 1.99 1.97 2.05 2.03 2.01 2.00 4.06 8.13 8.03 4.22 10.28 4.10
4.00 3.93 6.01
Chemical Shift (ppm)


DMSO-d6
171.87 170.98 160.02 149.70 146.74 144.35 143.48 132.94 132.83 130.83 130.25 129.14 129.04 128.58 128.08 124.11 121.90 119.35 114.04
74.26 74.16 71.22 70.72
55.36
40.01 39.84 39.68 39.51 39.34 39.18 39.02
OTf
AuL
N
OMe
4f, L= DPPF
13C NMR (125 MHz), DMSO-d6
Chemical Shift (ppm)

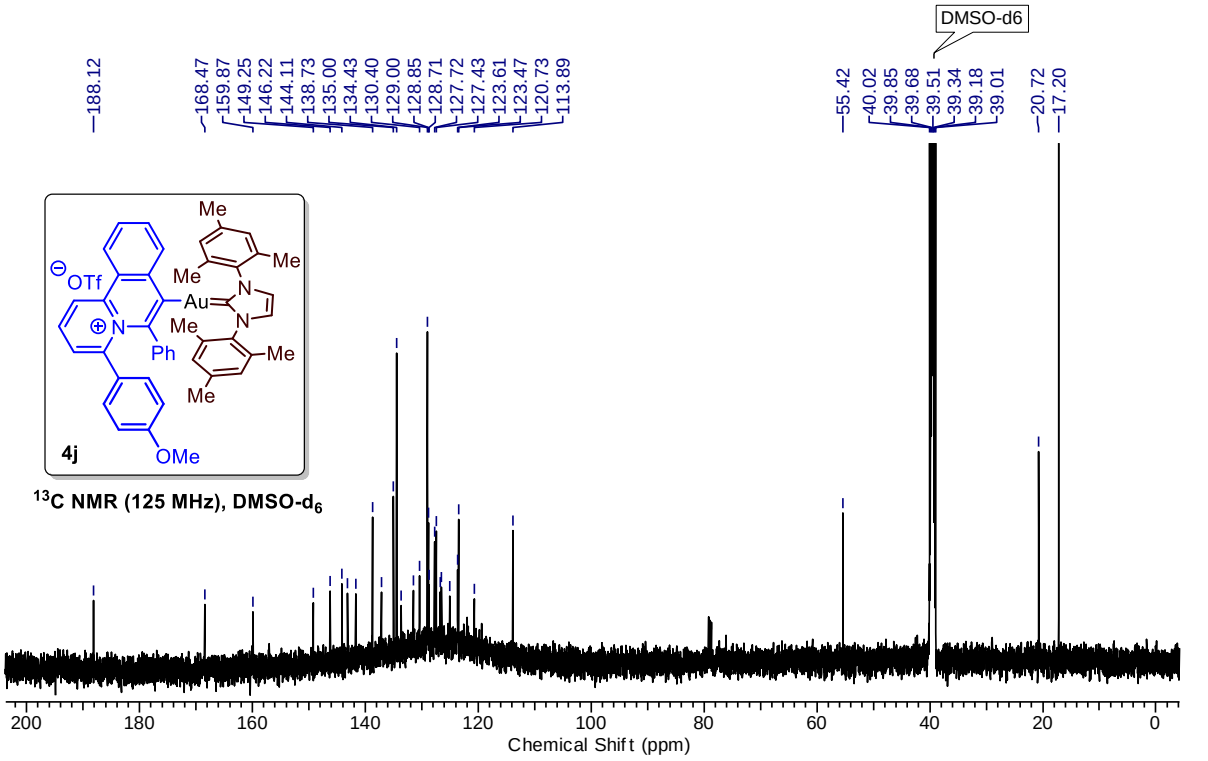

DMSO-d6
9.35
9.33
9.05
9.03
8.50
8.48
8.22
7.90
7.79
7.77
6.96
6.95
6.92
6.90
6.89
6.80
6.78
6.74
6.72
6.56
3.75
3.32
2.50
2.28
2.08
OTf
AuL
N
OMe
4g, L= P(trimesityl)
1H NMR (400 MHz), DMSO-d6
1.00 1.00 1.00 1.00 1.00 1.00 1.03 9.13 2.05 2.03 2.00
3.00
9.11 18.02
Chemical Shift (ppm)
DMSO-d6
167.11
160.04
149.67
146.71
142.42
142.31
140.57
140.55
132.32
131.37
131.28
129.08
128.43
127.73
125.83
125.38
120.87
114.01
55.45
40.14
39.93
39.72
39.51
39.31
39.09
38.88
23.62
23.52
20.36
OTf
AuL
N
OMe
4g, L= P(trimesetyl)
13C NMR (100 MHz), DMSO-d6
Chemical Shift (ppm)


DMSO-d6
9.42
9.40
9.12
9.10
8.63
8.62
8.54
8.52
7.97
7.95
7.85
7.24
7.23
7.22
7.20
7.12
7.08
7.06
7.05
7.00
6.77
3.80
3.74
3.31
2.50
OTf
AuL
N
OMe
4h, L= P(4-OMe-C6H4)3
1H NMR (500 MHz), DMSO-d6
1.00 1.00 1.01 1.01 1.02 1.02 1.01 6.08 2.07 9.01 2.05 2.00
9.03 3.00
Chemical Shift (ppm)
162.23
160.56
150.15
147.27
143.95
140.96
135.70
135.55
130.81
129.77
129.09
128.56
127.67
121.64
121.05
115.61
115.49
114.59
55.94
40.64
40.43
40.22
40.01
39.80
39.60
39.38
4h, L= P(4-OMe-C6H4)3
13C NMR (100 MHz), DMSO-d6
Chemical Shift (ppm)

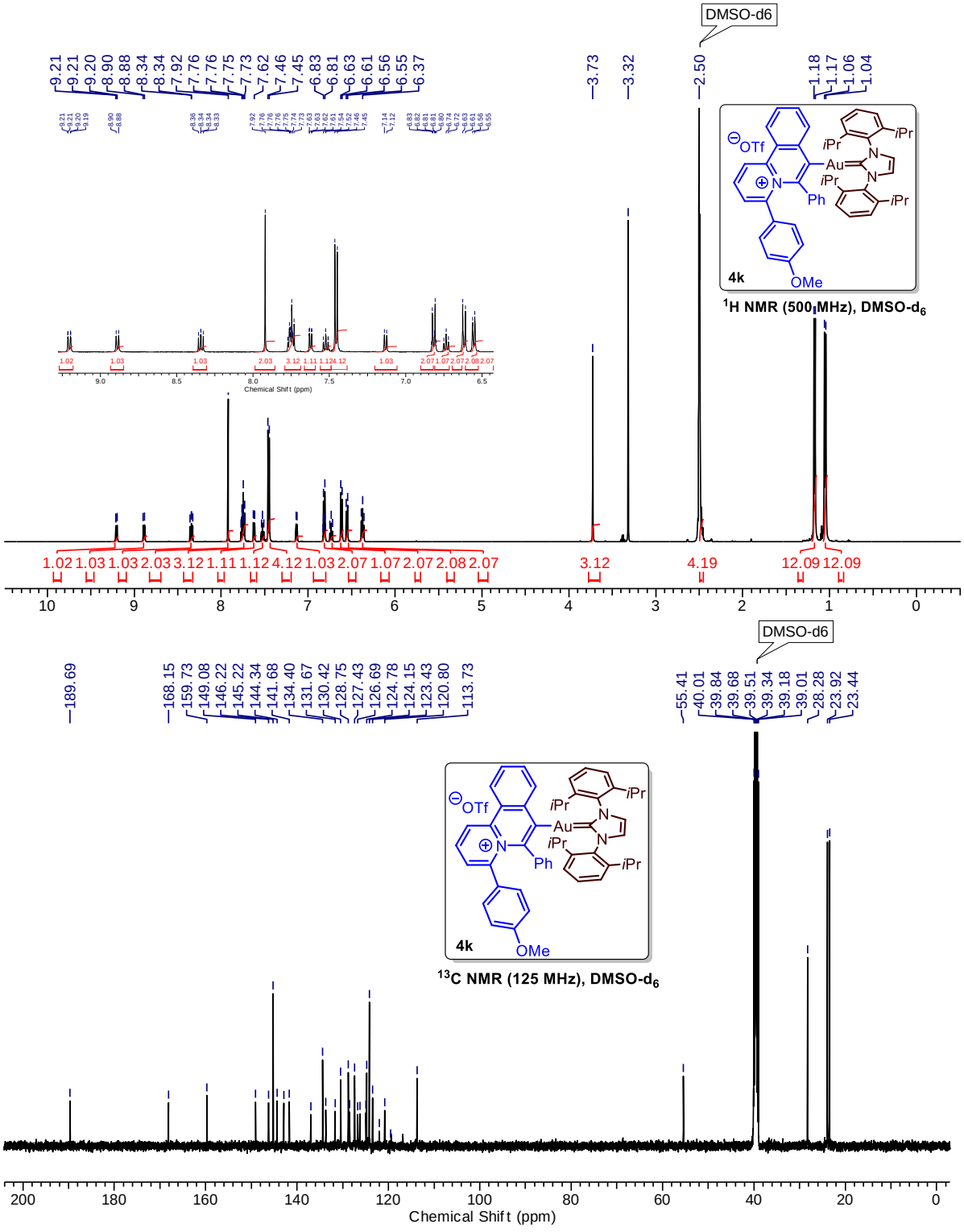

DMSO-d6
9.23 9.21 8.91 8.90 8.36 8.35 7.79 7.78 7.69 7.65 7.62 7.02 6.84 6.82 6.70 6.69 6.66 6.64 6.51 6.50
4.01 3.74 3.32 2.50 2.50 2.50 2.30 2.23
1.00 1.00 1.00 1.00 1.01 1.00 1.00 4.00 1.02 2.01 2.02 2.01 2.00 4.00 3.01 6.01 12.03
Chemical Shift (ppm)
4i
^{1}H NMR (500 MHz), DMSO-d$_6$
DMSO-d6
208.98 168.35 159.80 149.21 137.69 137.13 135.49 135.09 131.40 129.19 128.78 127.65 127.41 126.47 123.56 120.68 113.81
55.38 50.66 40.14 39.93 39.72 39.51 39.30 39.09 38.88 20.63 17.42
4i
^{13}C NMR (100 MHz), DMSO-d$_6$
Chemical Shift (ppm)

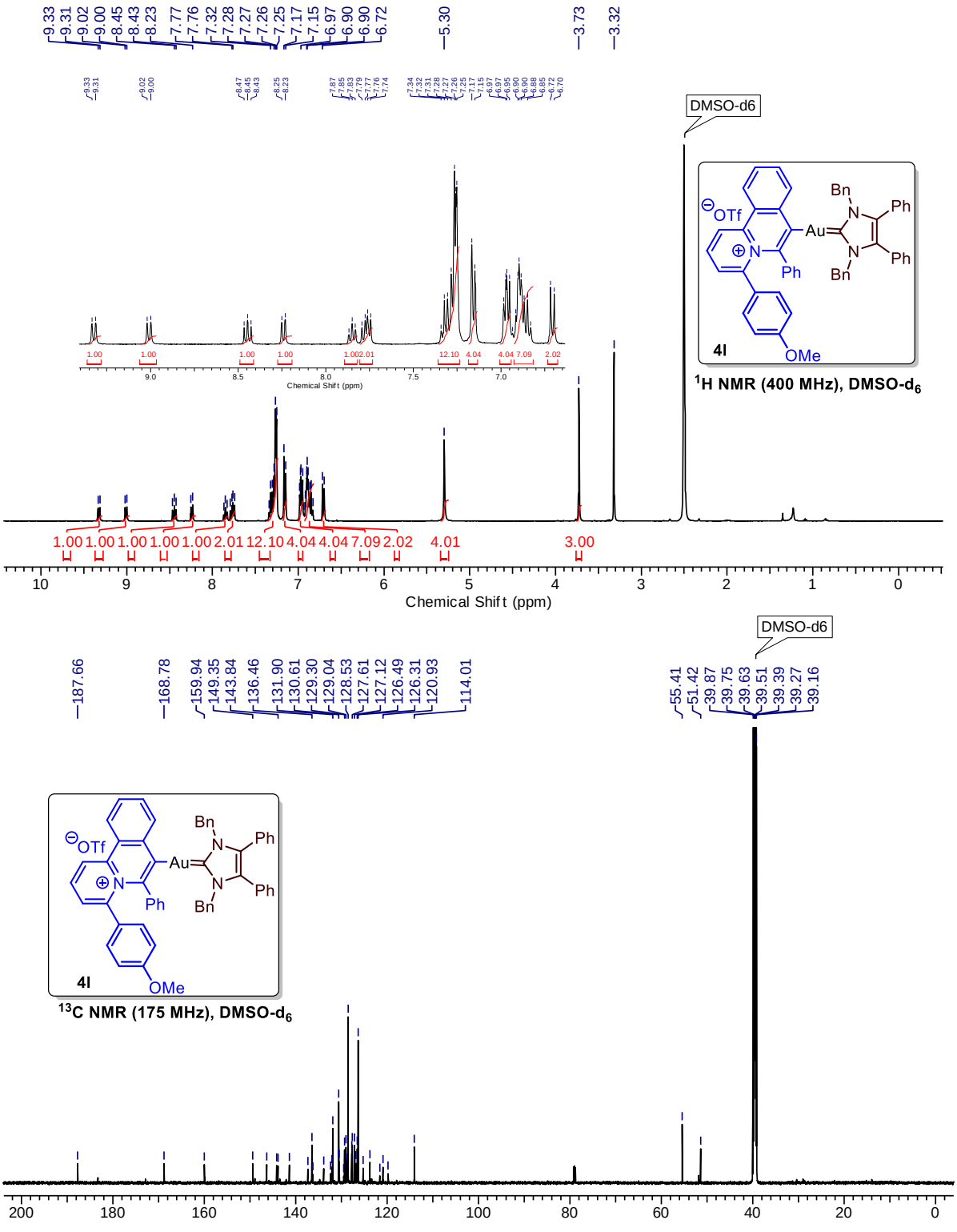


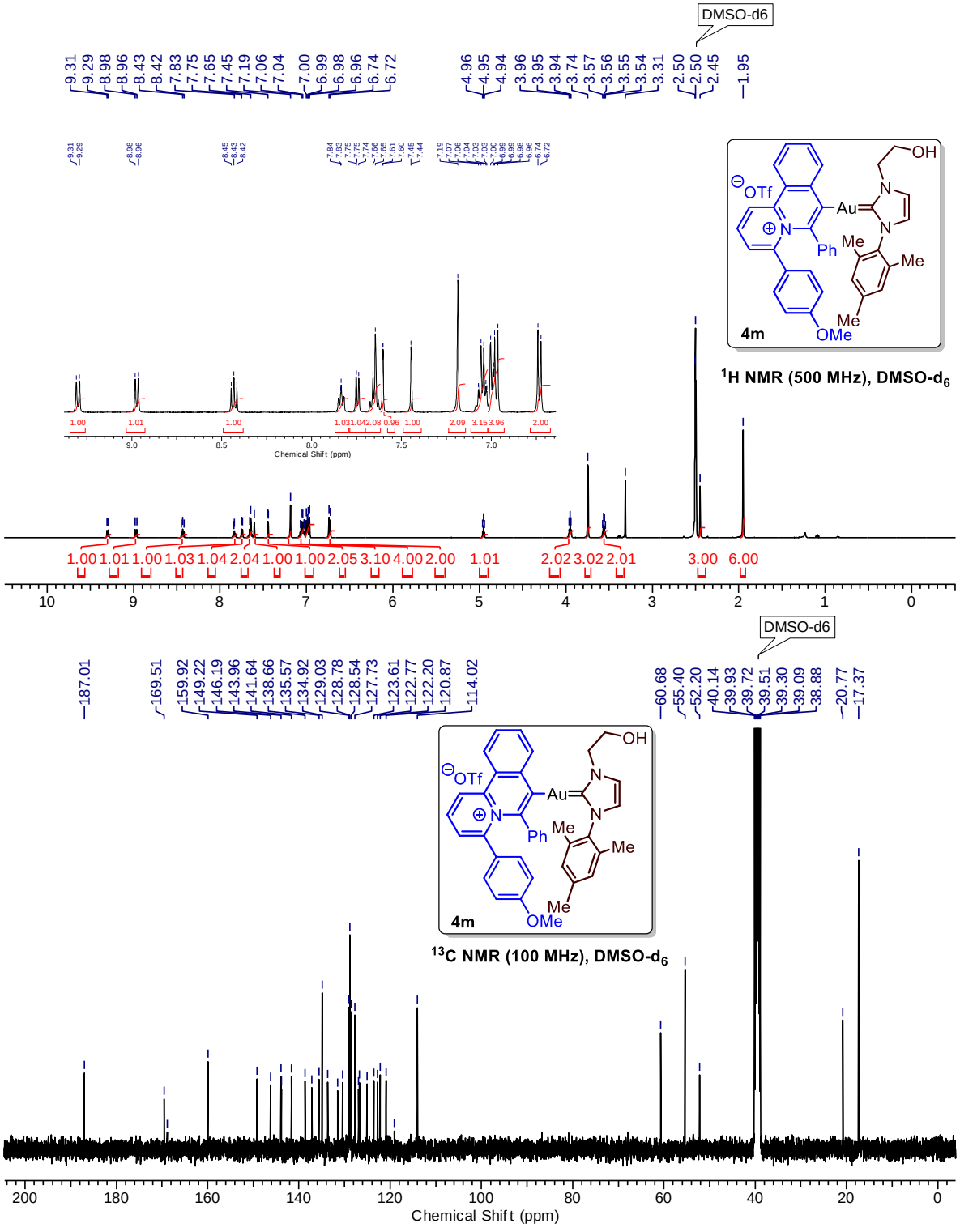
^{1}H NMR (700 MHz), DMSO-d_6

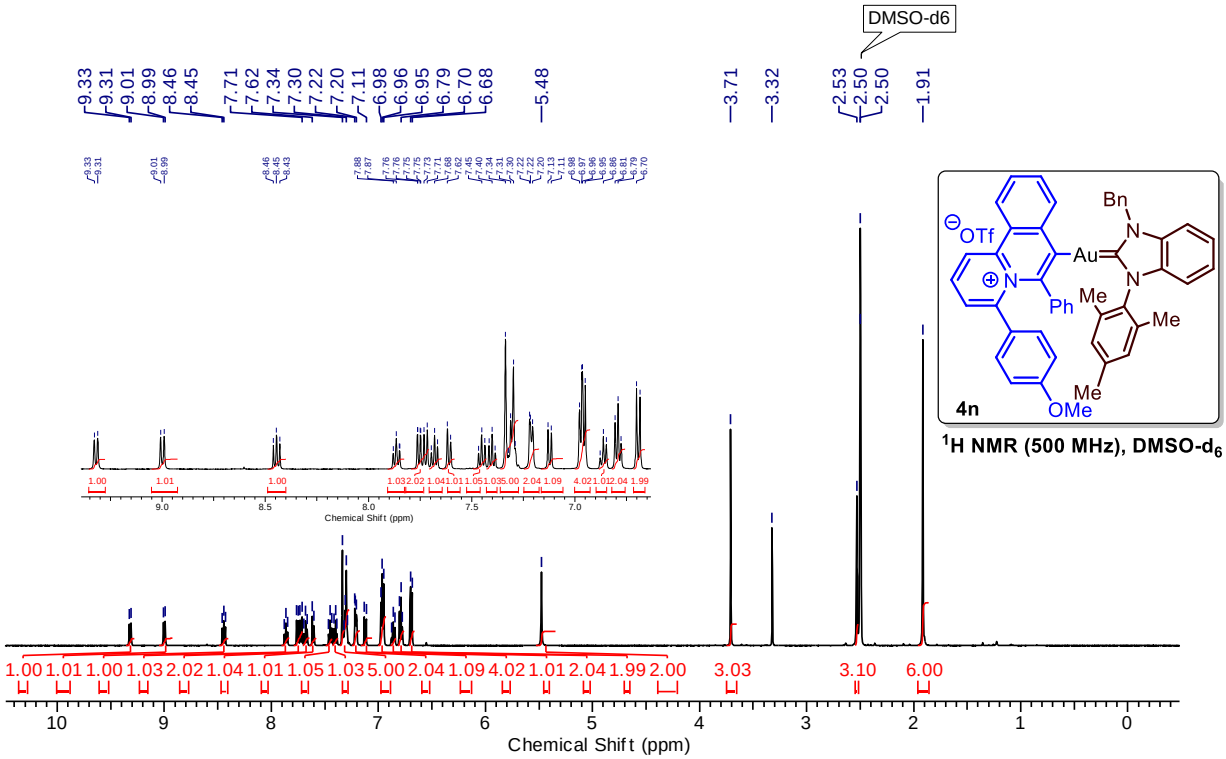


^{13}C NMR (125 MHz), DMSO-d_6

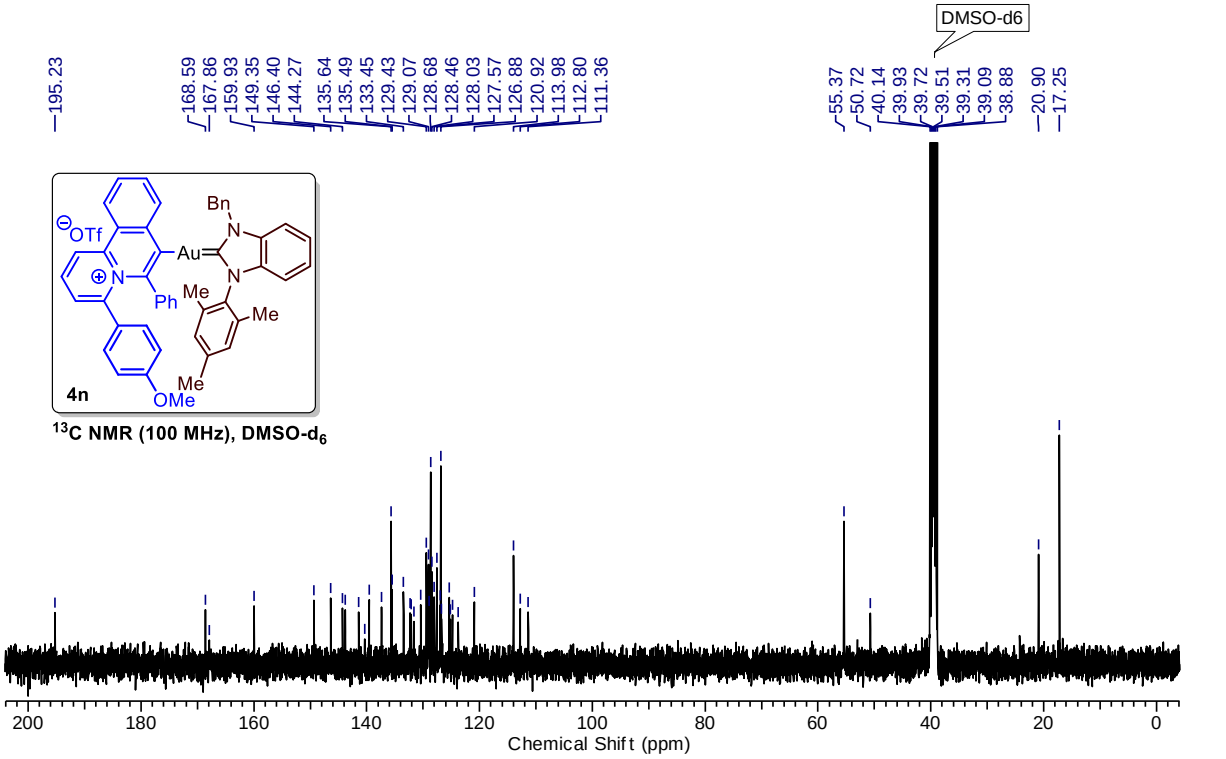

DMSO-d6
9.21
9.21
9.20
8.90
8.88
8.34
8.34
7.92
7.76
7.76
7.75
7.73
7.62
7.46
7.45
6.83
6.81
6.63
6.61
6.56
6.55
6.37
3.73
3.32
2.50
1.18
1.17
1.06
1.04
OTf
iPr
Au
Ph
OMe
4k
1H NMR (500 MHz), DMSO-d6
1.02 1.03 1.03 2.03 3.12 1.11 1.12 4.12 1.03 2.07 1.07 2.07 2.08 2.07
3.12
4.19
12.09 12.09
Chemical Shift (ppm)
DMSO-d6
189.69
168.15
159.73
149.08
146.22
145.22
144.34
141.68
134.40
131.67
130.42
128.75
127.43
126.69
124.78
124.15
123.43
120.80
113.73
55.41
40.01
39.84
39.68
39.51
39.34
39.18
39.01
28.28
23.92
23.44
13C NMR (125 MHz), DMSO-d6
Chemical Shift (ppm)


DMSO-d6
4l
^{1}H NMR (400 MHz), DMSO-d$_6$
Chemical Shift (ppm)
DMSO-d6
4l
^{13}C NMR (175 MHz), DMSO-d$_6$

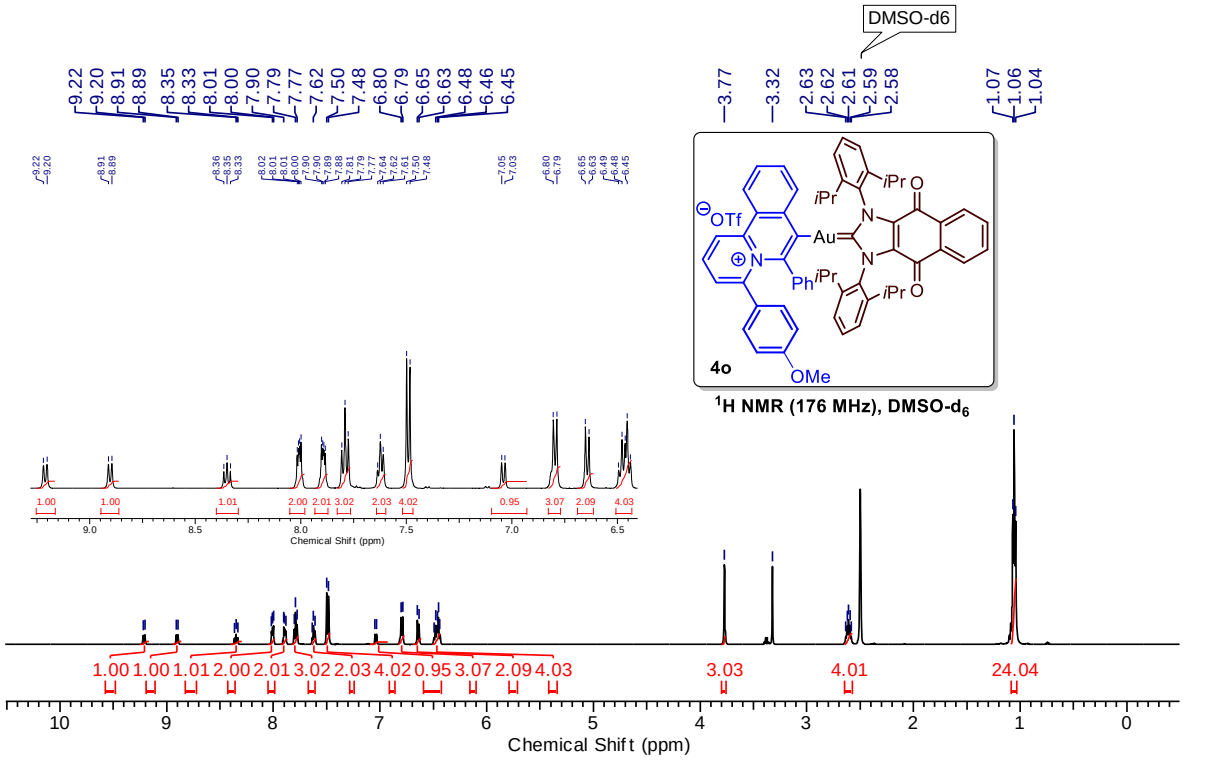

DMSO-d6
9.31 9.29 8.98 8.96 8.43 8.42 7.83 7.75 7.65 7.45 7.19 7.06 7.04 7.00 6.99 6.98 6.96 6.74 6.72
4.96 4.95 4.94 3.96 3.95 3.94 3.74 3.57 3.56 3.55 3.54 3.31 2.50 2.50 2.45 1.95
OH
OTf
Au
N
Ph
Me
Me
Me
4m
OMe
1H NMR (500 MHz), DMSO-d6
1.00 1.01 1.00 1.03 1.04 2.04 1.00 1.00 2.05 3.10 4.00 2.00 1.01 2.02 3.02 2.01 3.00 6.00
Chemical Shift (ppm)
DMSO-d6
187.01 169.51 159.92 149.22 146.19 143.96 141.64 138.66 135.57 134.92 129.03 128.78 128.54 127.73 123.61 122.77 122.20 120.87 114.02
60.68 55.40 52.20 40.14 39.93 39.72 39.51 39.30 39.09 38.88 20.77 17.37
13C NMR (100 MHz), DMSO-d6
Chemical Shift (ppm)



^{1}H NMR (500 MHz), DMSO-d_6



^{13}C NMR (100 MHz), DMSO-d_6


DMSO-d6
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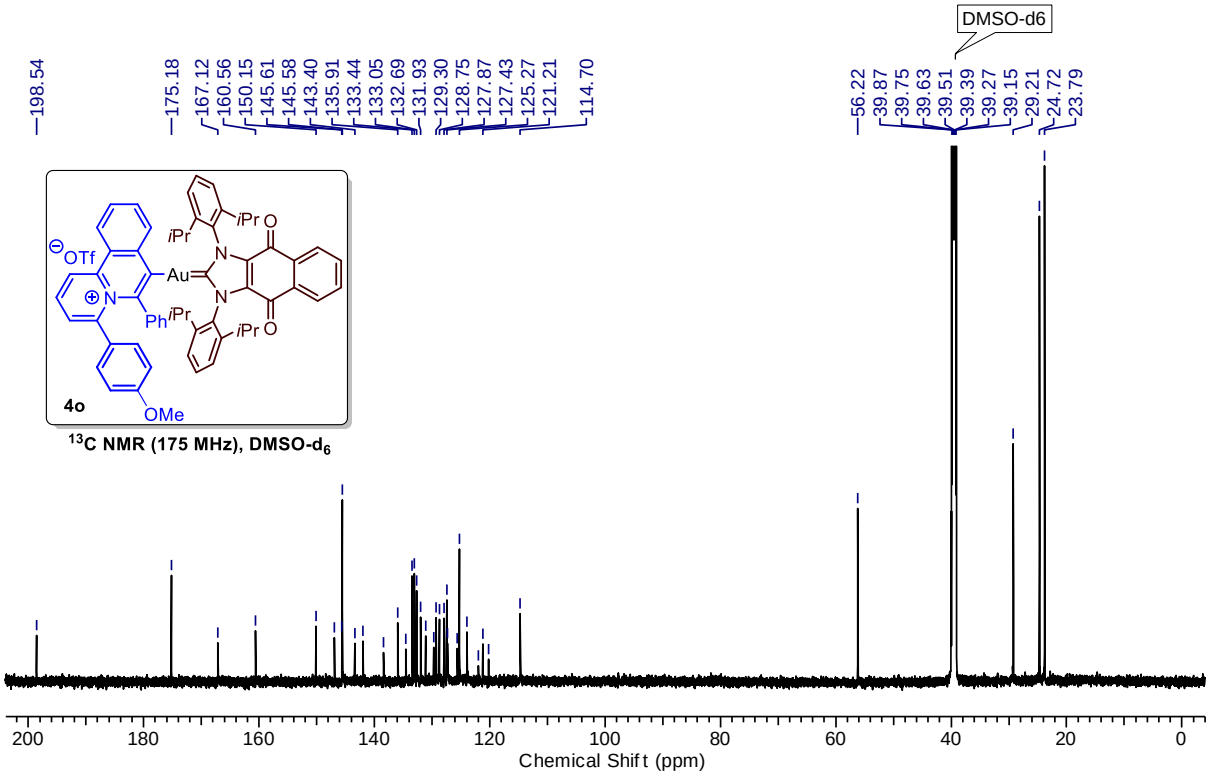
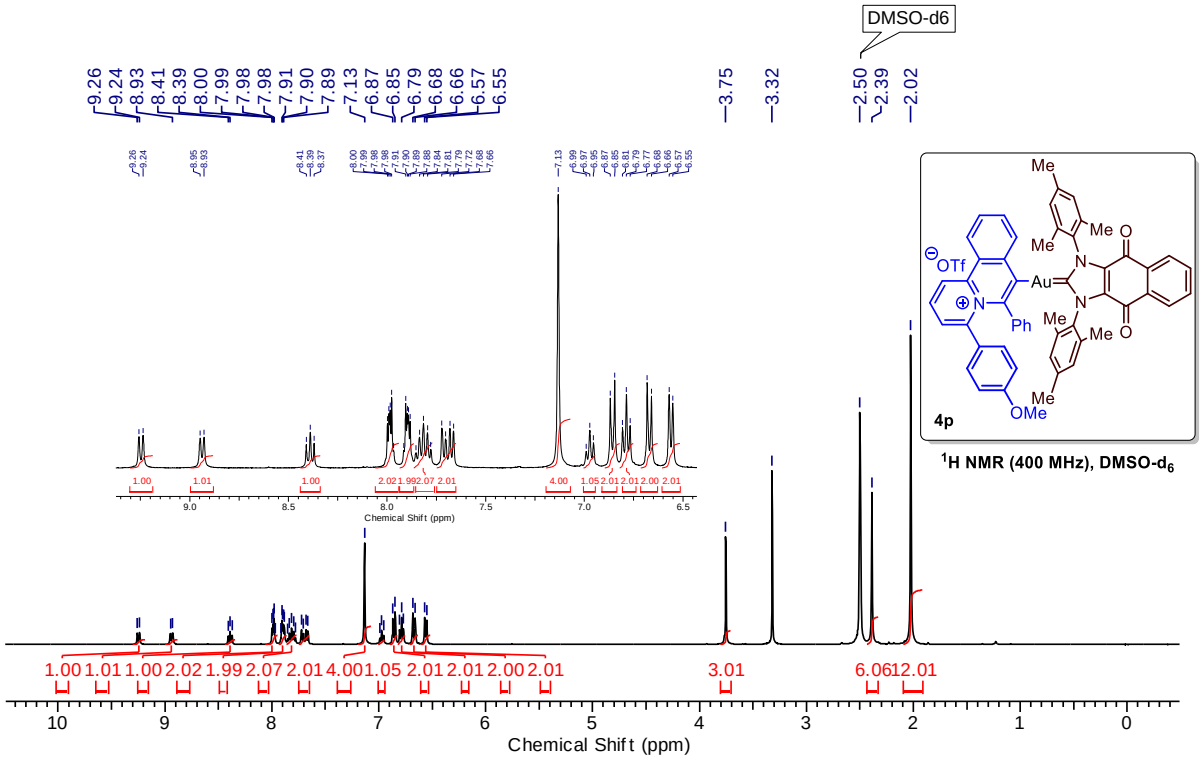
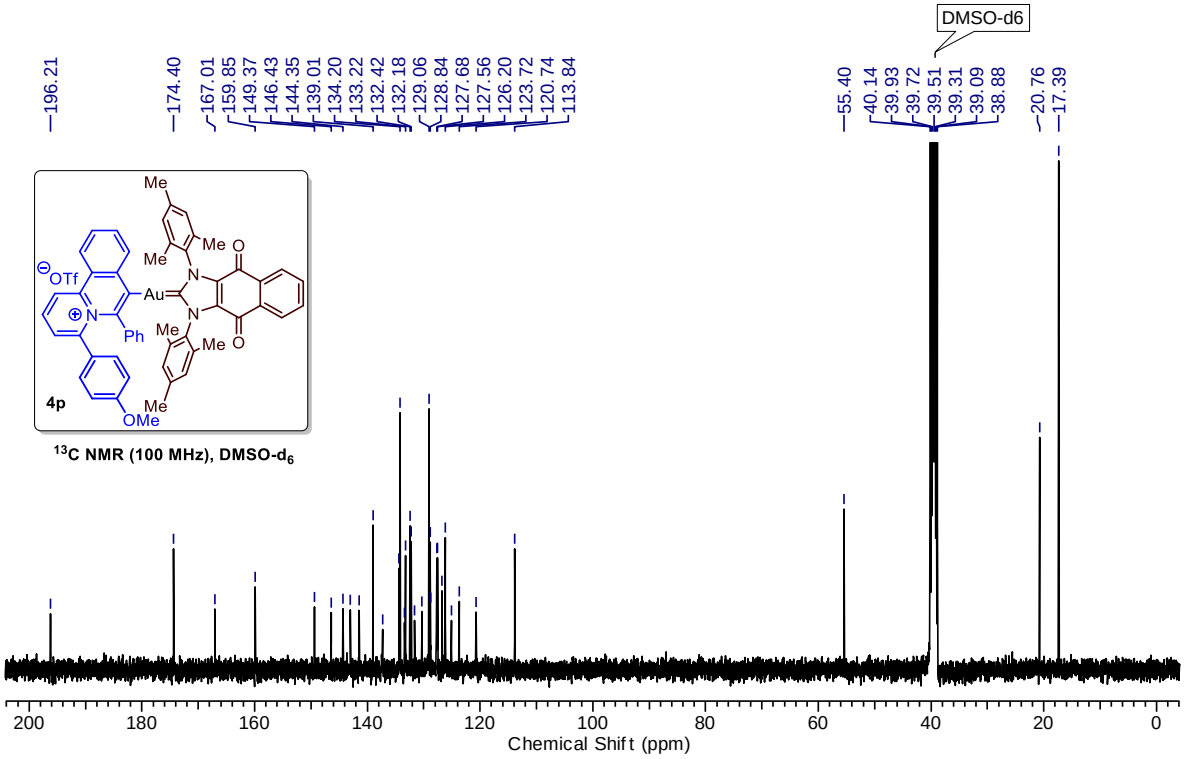
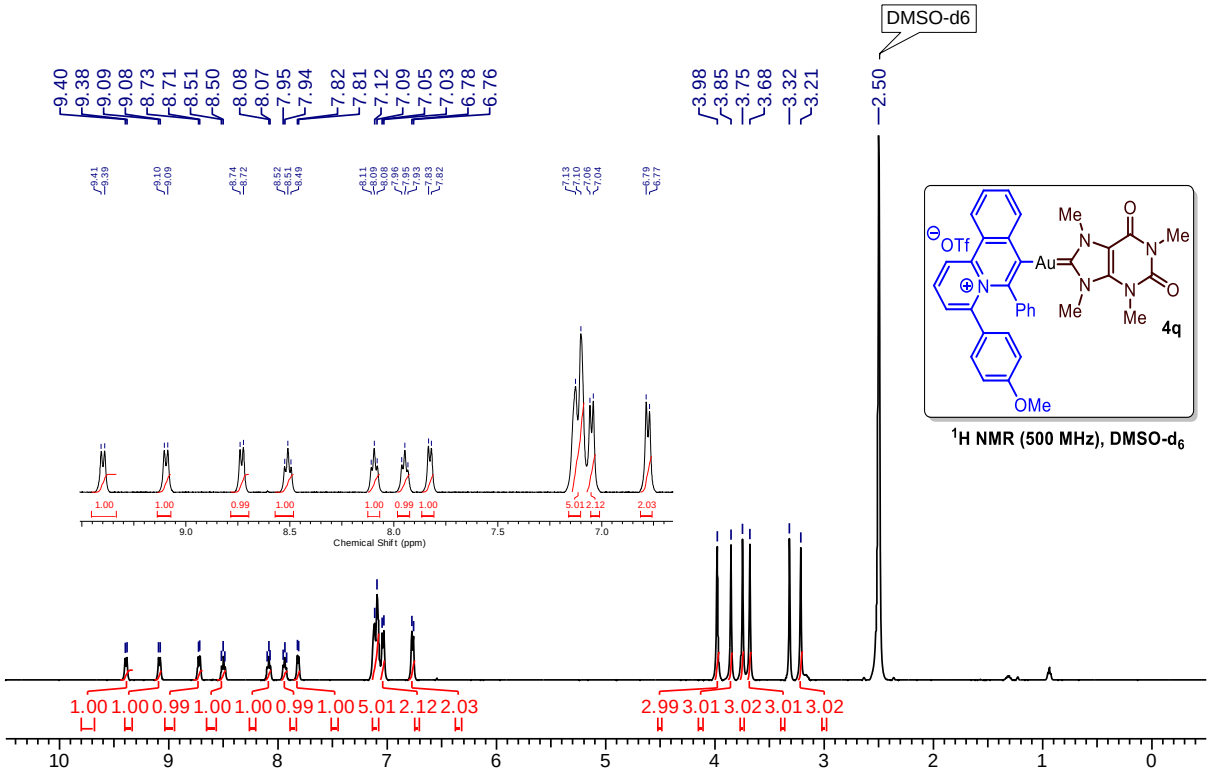
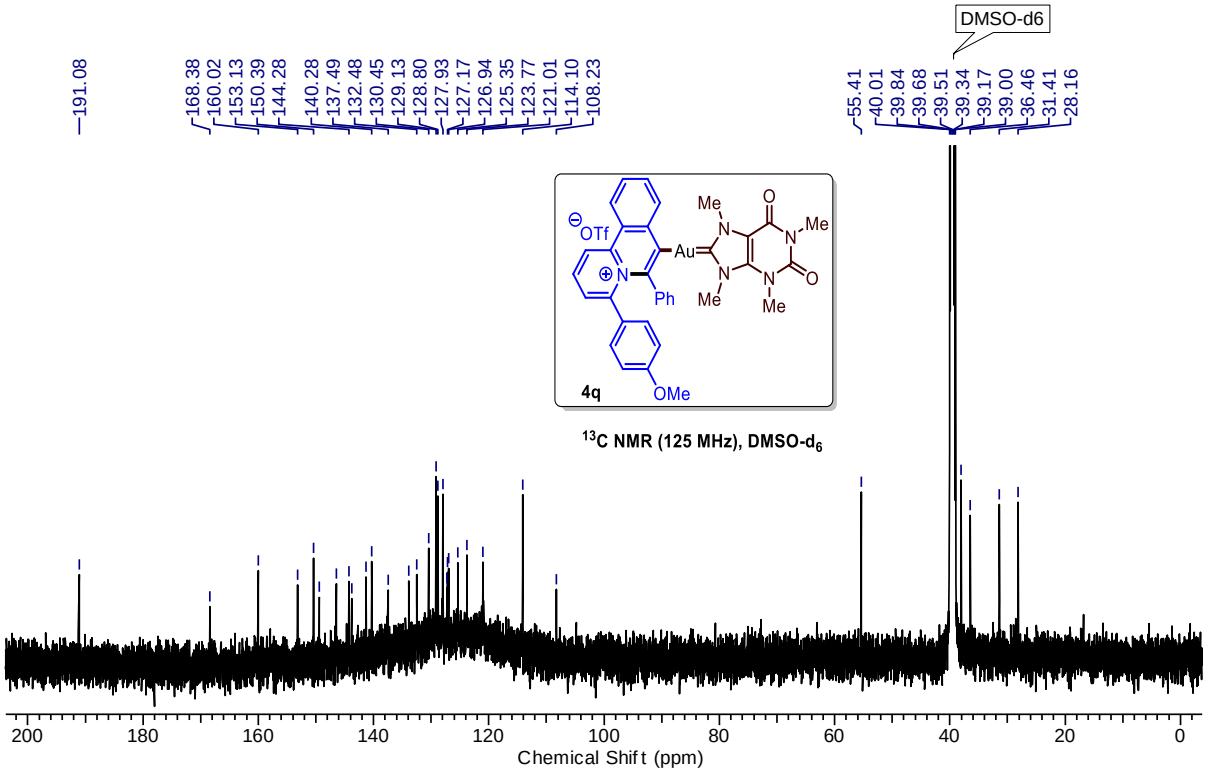
3.77 3.32 2.63 2.62 2.61 2.59 2.58 1.07 1.06 1.04
4o
1H NMR (176 MHz), DMSO-d6
1.00 1.00 1.01 2.00 2.01 3.02 2.03 4.02 0.95 3.07 2.09 4.03
3.03 4.01 24.04
Chemical Shift (ppm)

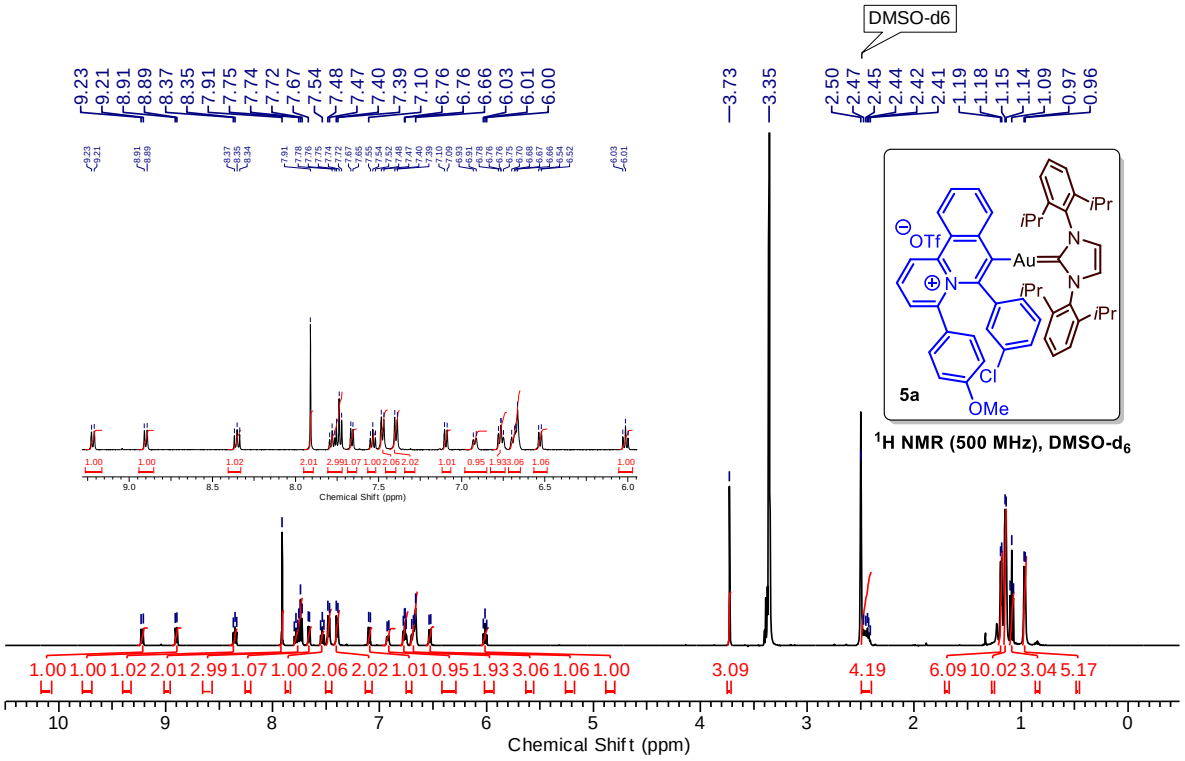

DMSO-d6
198.54 175.18 167.12 160.56 150.15 145.61 145.58 143.40 135.91 133.44 133.05 132.69 131.93 129.30 128.75 127.87 127.43 125.27 121.21 114.70
56.22 39.87 39.75 39.63 39.51 39.39 39.27 39.15 29.21 24.72 23.79
4o
13C NMR (175 MHz), DMSO-d6
Chemical Shift (ppm)

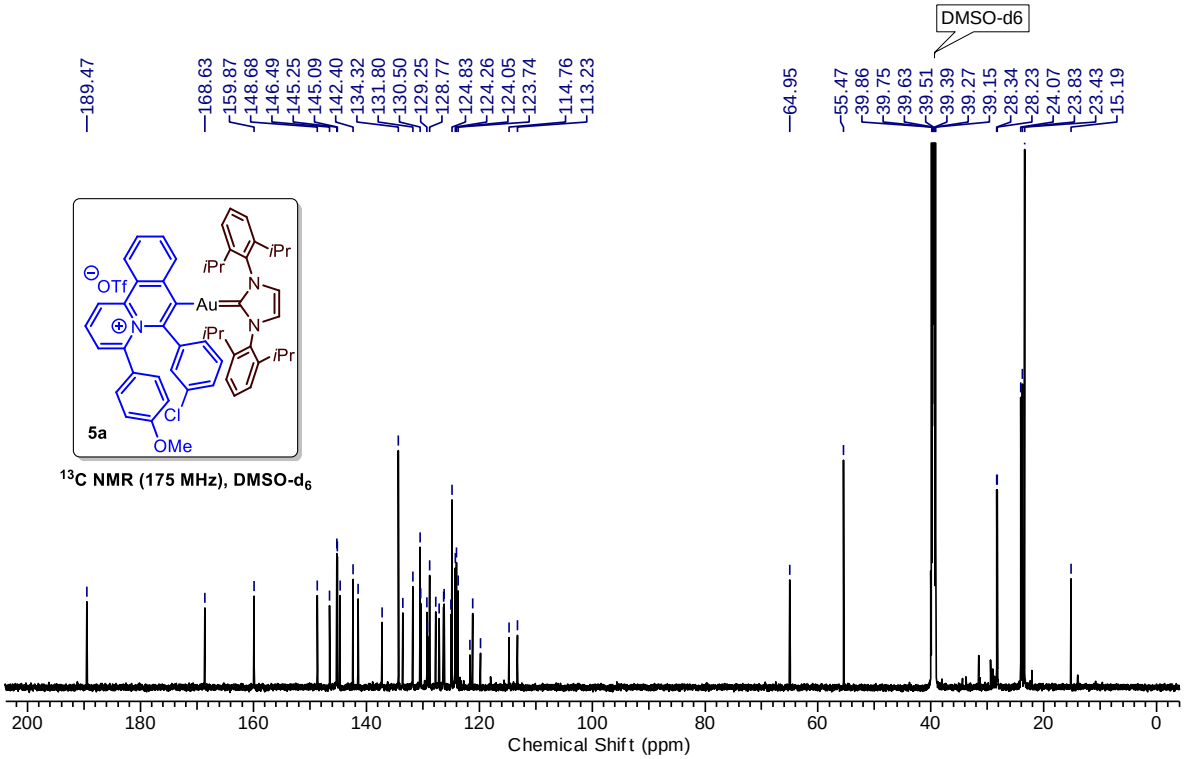

DMSO-d6
9.26
9.24
8.93
8.41
8.39
8.00
7.99
7.98
7.98
7.91
7.90
7.89
7.13
6.87
6.85
6.79
6.68
6.66
6.57
6.55
3.75
3.32
2.50
2.39
2.02
4p
1H NMR (400 MHz), DMSO-d6
1.00 1.01 1.00 2.02 1.99 2.07 2.01 4.00 1.05 2.01 2.01 2.00 2.01
3.01
6.06 12.01
Chemical Shift (ppm)

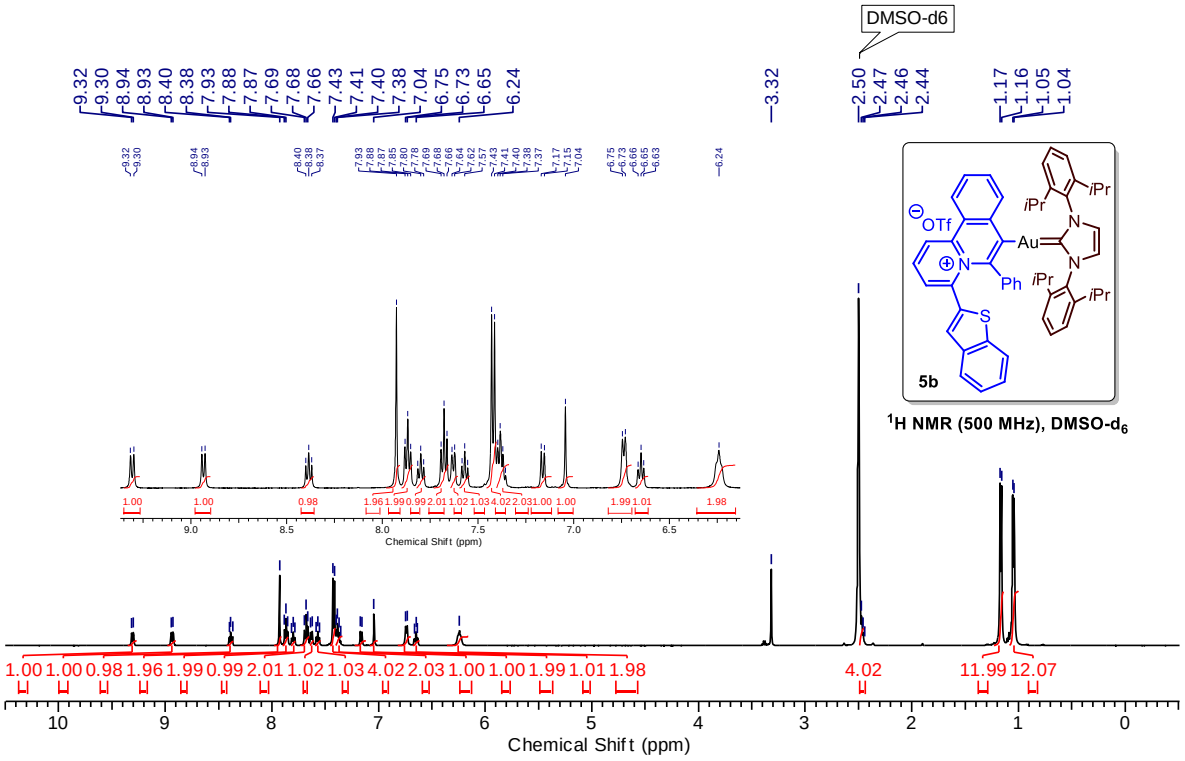

DMSO-d6
196.21
174.40
167.01
159.85
149.37
146.43
144.35
139.01
134.20
133.22
132.42
132.18
129.06
128.84
127.68
127.56
126.20
123.72
120.74
113.84
55.40
40.14
39.93
39.72
39.51
39.31
39.09
38.88
20.76
17.39
4p
13C NMR (100 MHz), DMSO-d6
Chemical Shift (ppm)

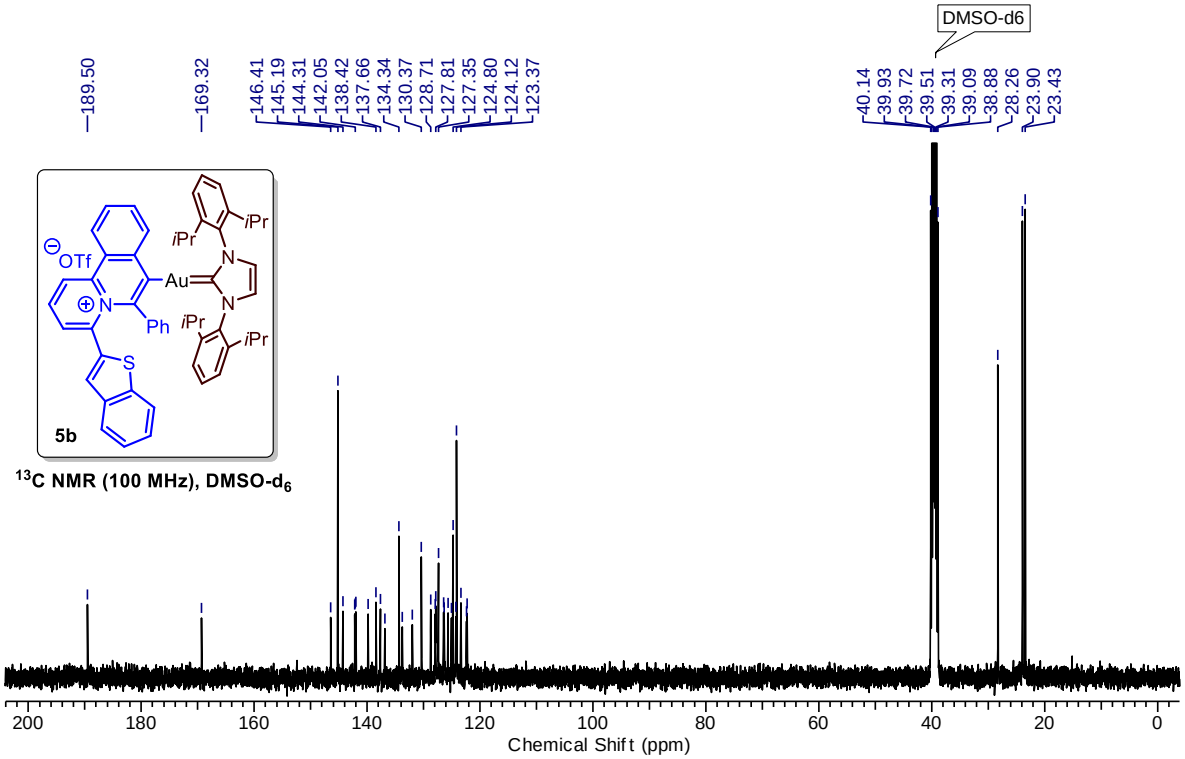

DMSO-d6
9.40 9.38 9.09 9.08 8.73 8.71 8.51 8.50 8.08 8.07 7.95 7.94 7.82 7.81 7.12 7.09 7.05 7.03 6.78 6.76
3.98 3.85 3.75 3.68 3.32 3.21
2.50
1.00 1.00 0.99 1.00 1.00 0.99 1.00 5.01 2.12 2.03
2.99 3.01 3.02 3.01 3.02
Chemical Shift (ppm)
4q
^{1}H NMR (500 MHz), DMSO-d$_6$

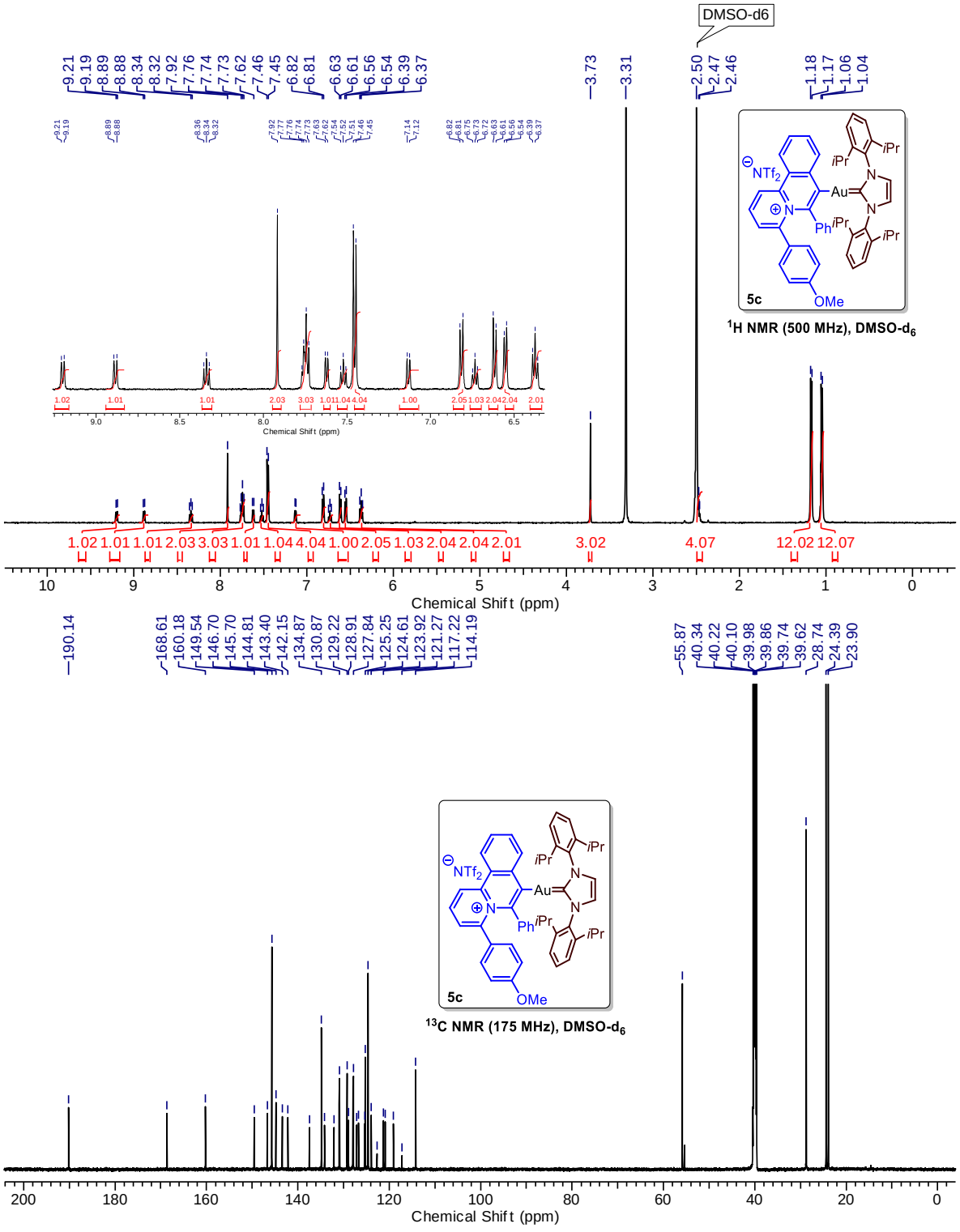

DMSO-d6
191.08
168.38 160.02 153.13 150.39 144.28 140.28 137.49 132.48 130.45 129.13 128.80 127.93 127.17 126.94 125.35 123.77 121.01 114.10 108.23
55.41 40.01 39.84 39.68 39.51 39.34 39.17 39.00 36.46 31.41 28.16
4q
^{13}C NMR (125 MHz), DMSO-d$_6$
Chemical Shift (ppm)

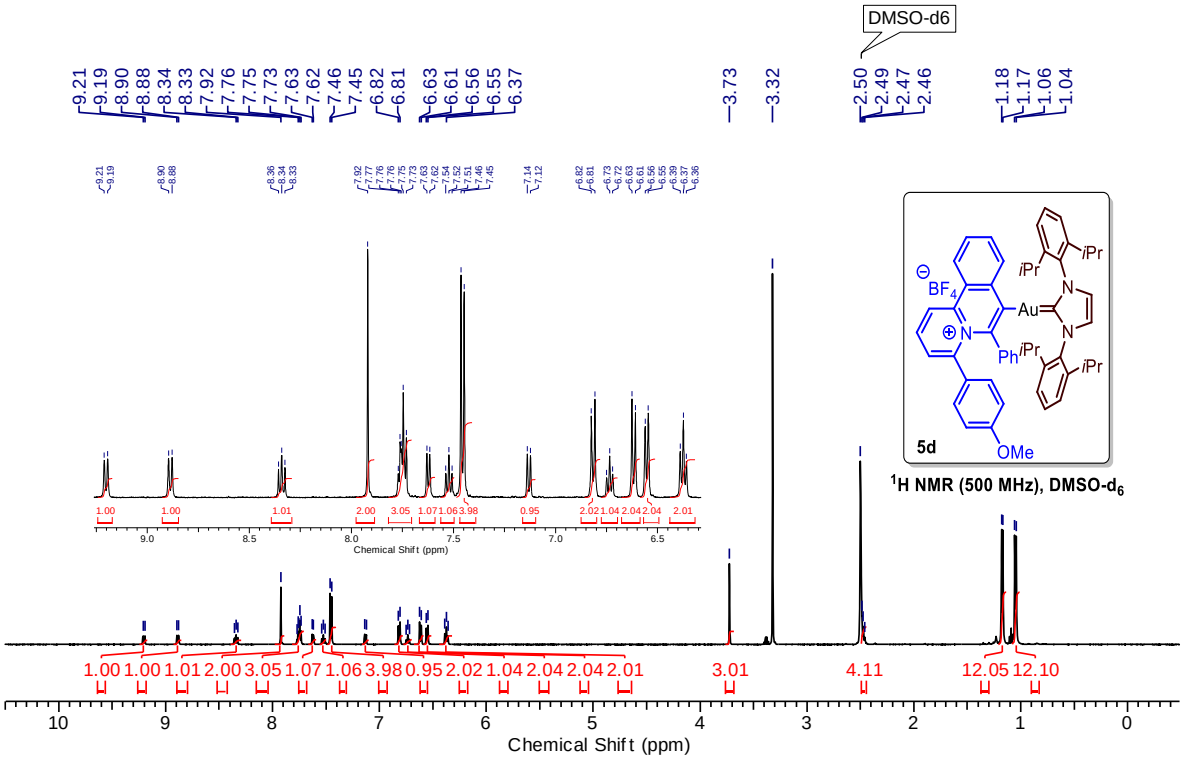

DMSO-d6
9.23 9.21 8.91 8.89 8.37 8.35 7.91 7.75 7.74 7.72 7.67 7.54 7.48 7.47 7.40 7.39 7.10 6.76 6.76 6.66 6.03 6.01 6.00
3.73 3.35
2.50 2.47 2.45 2.44 2.42 2.41 1.19 1.18 1.15 1.14 1.09 0.97 0.96
OTf
Au
iPr
Cl
OMe
5a
1H NMR (500 MHz), DMSO-d6
1.00 1.00 1.02 2.01 2.99 1.07 1.00 2.06 2.02 1.01 0.95 1.93 3.06 1.06 1.00
3.09
4.19
6.09 10.02 3.04 5.17
Chemical Shift (ppm)

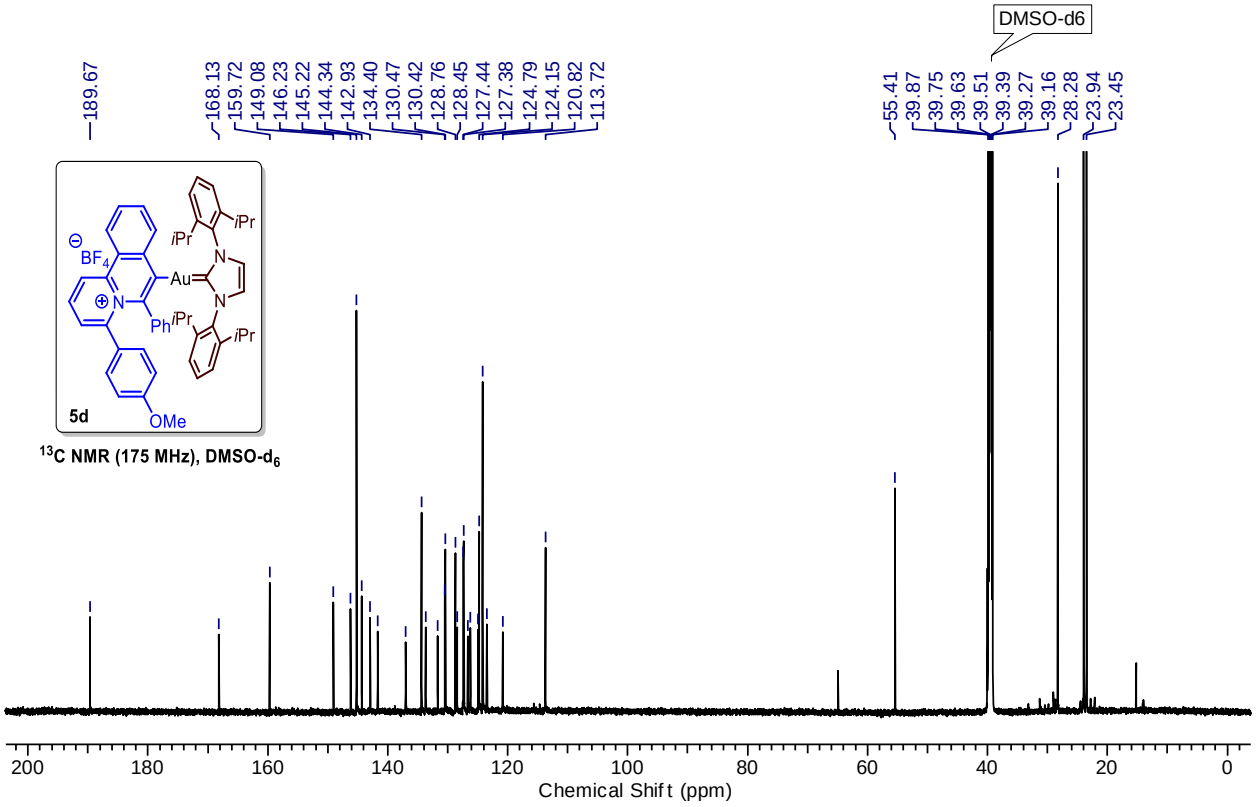

DMSO-d6
189.47
168.63 159.87 148.68 146.49 145.25 145.09 142.40 134.32 131.80 130.50 129.25 128.77 124.83 124.26 124.05 123.74 114.76 113.23
64.95
55.47 39.86 39.75 39.63 39.51 39.39 39.27 39.15 28.34 28.23 24.07 23.83 23.43 15.19
OTf
Au
iPr
Cl
OMe
5a
13C NMR (175 MHz), DMSO-d6
Chemical Shift (ppm)

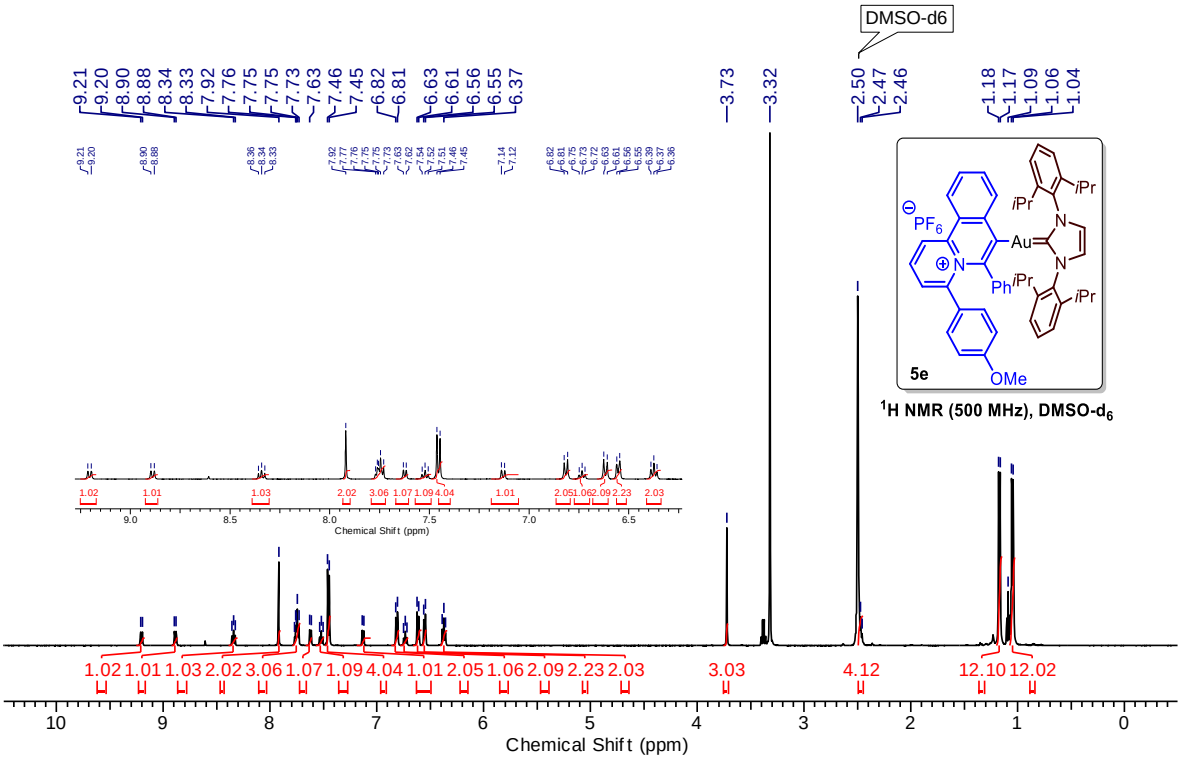

DMSO-d6
9.32 9.30 8.94 8.93 8.40 8.38 7.93 7.88 7.87 7.69 7.68 7.66 7.43 7.41 7.40 7.38 7.04 6.75 6.73 6.65 6.24
3.32
2.50 2.47 2.46 2.44
1.17 1.16 1.05 1.04
OTf
Au
Ph
iPr
S
5b
1H NMR (500 MHz), DMSO-d6
1.00 1.00 0.98 1.96 1.99 0.99 2.01 1.02 1.03 4.02 2.03 1.00 1.00 1.99 1.01 1.98
4.02
11.99 12.07
Chemical Shift (ppm)

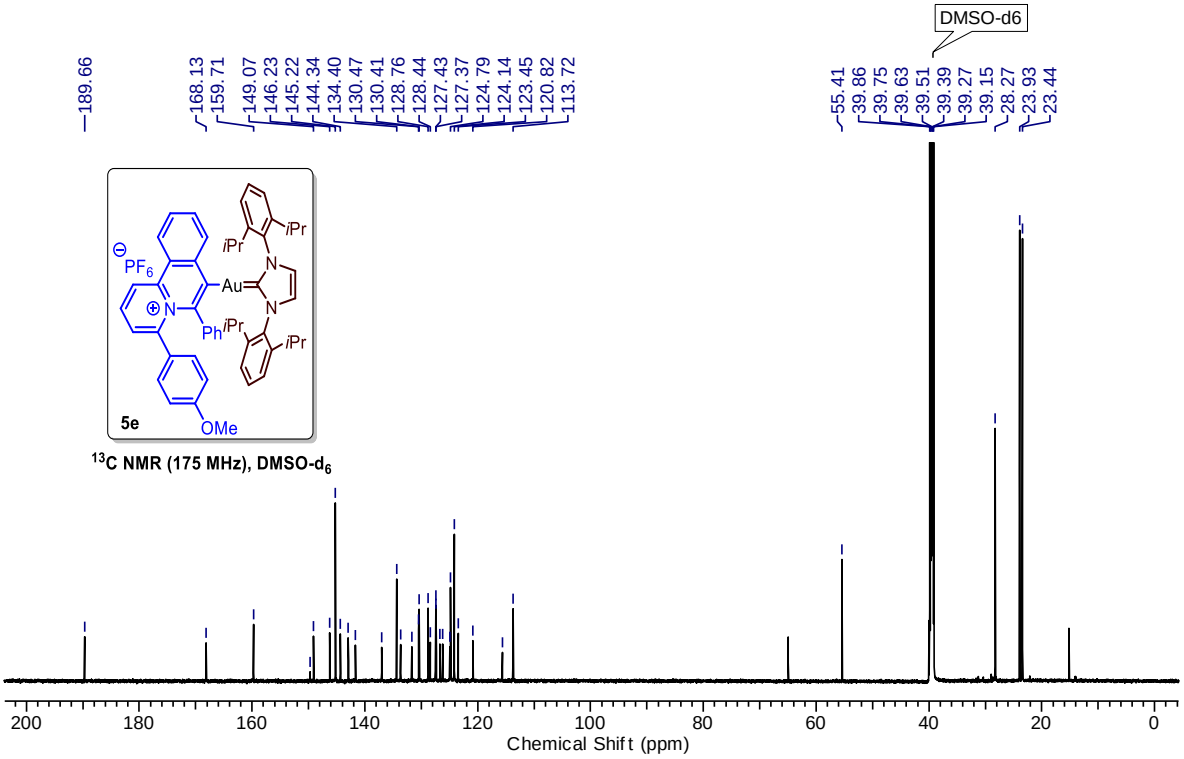

DMSO-d6
189.50
169.32
146.41 145.19 144.31 142.05 138.42 137.66 134.34 130.37 128.71 127.81 127.35 124.80 124.12 123.37
40.14 39.93 39.72 39.51 39.31 39.09 38.88 28.26 23.90 23.43
OTf
Au
Ph
iPr
S
5b
13C NMR (100 MHz), DMSO-d6
Chemical Shift (ppm)

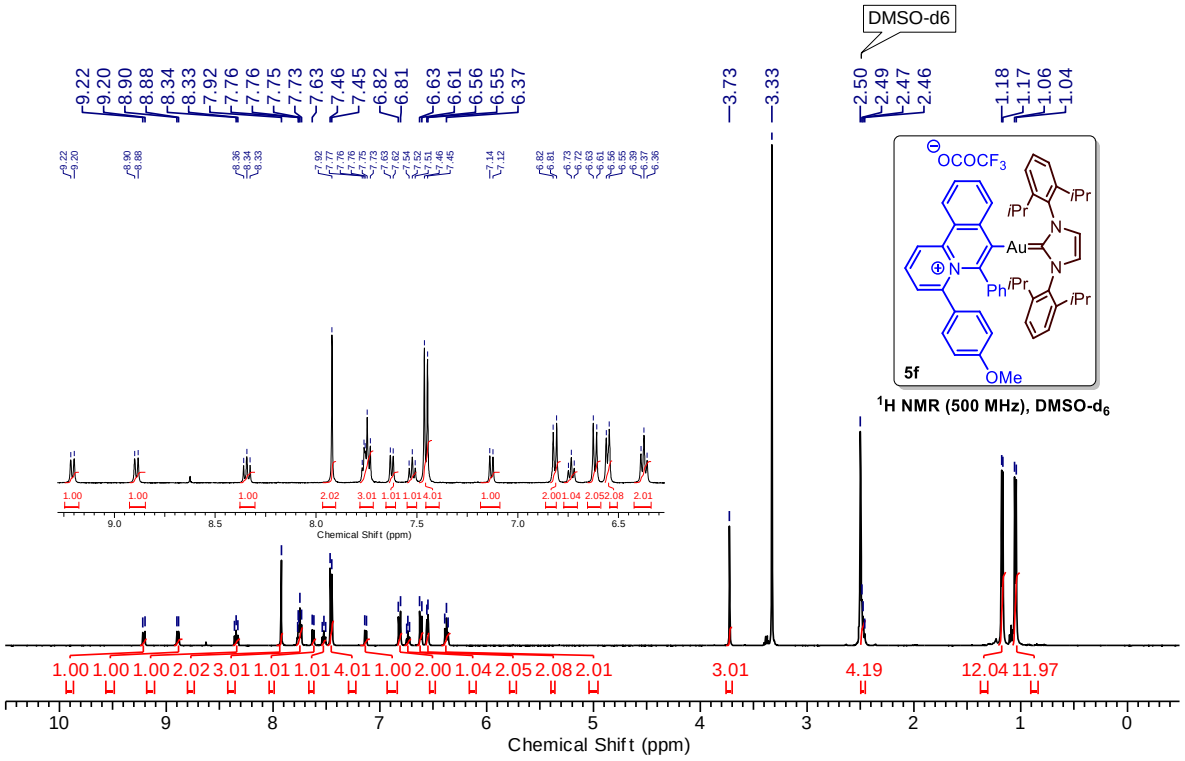

DMSO-d6
9.21 9.19 8.89 8.88 8.34 8.32 7.92 7.76 7.74 7.73 7.62 7.46 7.45 6.82 6.81 6.63 6.61 6.56 6.54 6.39 6.37
3.73 3.31
2.50 2.47 2.46
1.18 1.17 1.06 1.04
1.02 1.01 1.01 2.03 3.03 1.01 1.04 4.04 1.00 2.05 1.03 2.04 2.04 2.01
3.02
4.07
12.02 12.07
Chemical Shift (ppm)
5c
1H NMR (500 MHz), DMSO-d6
190.14
168.61 160.18 149.54 146.70 145.70 144.81 143.40 142.15 134.87 130.87 129.22 128.91 127.84 125.25 124.61 123.92 121.27 117.22 114.19
55.87 40.34 40.22 40.10 39.98 39.86 39.74 39.62 28.74 24.39 23.90
Chemical Shift (ppm)
5c
13C NMR (175 MHz), DMSO-d6

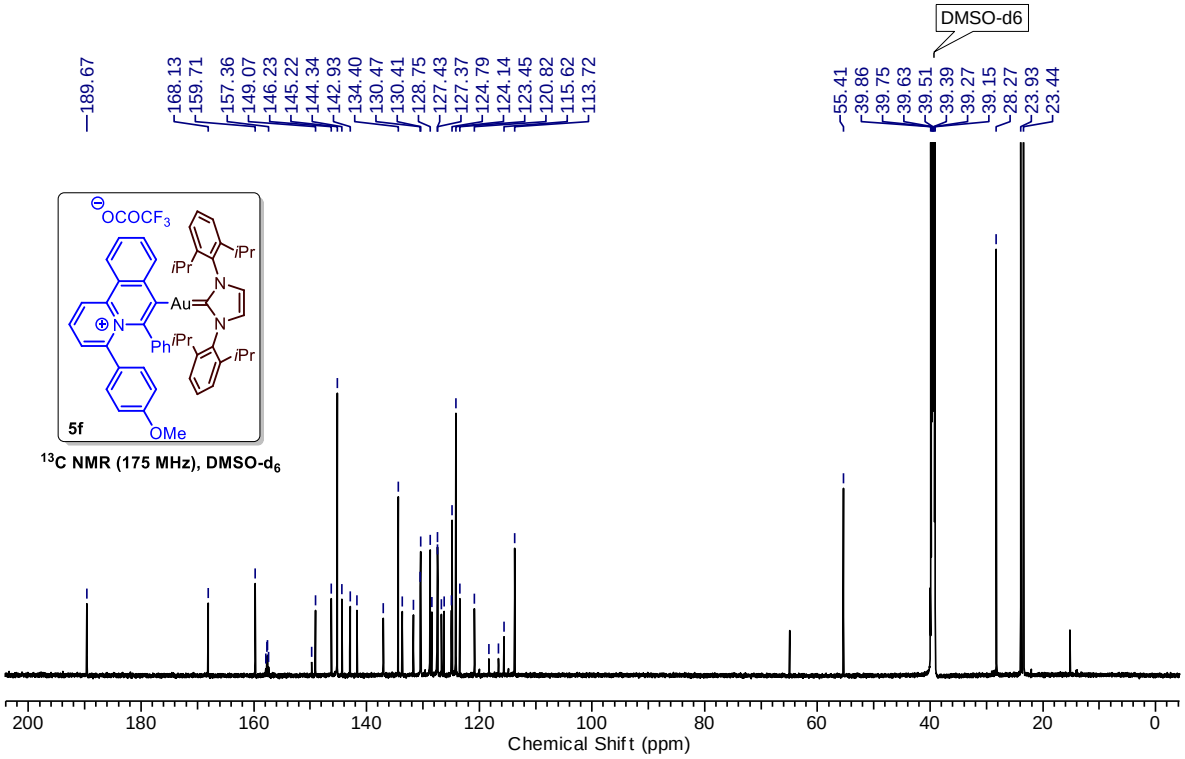

DMSO-d6
9.21
9.19
8.90
8.88
8.34
8.33
7.92
7.76
7.75
7.73
7.63
7.62
7.46
7.45
6.82
6.81
6.63
6.61
6.56
6.55
6.37
3.73
3.32
2.50
2.49
2.47
2.46
1.18
1.17
1.06
1.04
1.00 1.00 1.01 2.00 3.05 1.07 1.06 3.98 0.95 2.02 1.04 2.04 2.04 2.01
3.01
4.11
12.05 12.10
Chemical Shift (ppm)
5d
^{1}H NMR (500 MHz), DMSO-d_6


DMSO-d6
189.67
168.13
159.72
149.08
146.23
145.22
144.34
142.93
134.40
130.47
130.42
128.76
128.45
127.44
127.38
124.79
124.15
120.82
113.72
55.41
39.87
39.75
39.63
39.51
39.39
39.27
39.16
28.28
23.94
23.45
Chemical Shift (ppm)
5d
^{13}C NMR (175 MHz), DMSO-d_6


DMSO-d6
9.21 9.20 8.90 8.88 8.34 8.33 7.92 7.76 7.75 7.75 7.73 7.63 7.46 7.45 6.82 6.81 6.63 6.61 6.56 6.55 6.37
3.73 3.32
2.50 2.47 2.46
1.18 1.17 1.09 1.06 1.04
PF6
Au
Ph
iPr
OMe
5e
1H NMR (500 MHz), DMSO-d6
1.02 1.01 1.03 2.02 3.06 1.07 1.09 4.04 1.01 2.05 1.06 2.09 2.23 2.03
3.03
4.12
12.10 12.02
Chemical Shift (ppm)


DMSO-d6
189.66
168.13 159.71 149.07 146.23 145.22 144.34 134.40 130.47 130.41 128.76 128.44 127.43 127.37 124.79 124.14 123.45 120.82 113.72
55.41 39.86 39.75 39.63 39.51 39.39 39.27 39.15 28.27 23.93 23.44
PF6
Au
Ph
iPr
OMe
5e
13C NMR (175 MHz), DMSO-d6
Chemical Shift (ppm)


DMSO-d6
9.22 9.20 8.90 8.88 8.34 8.33 7.92 7.76 7.76 7.75 7.73 7.63 7.46 7.45 6.82 6.81 6.63 6.61 6.56 6.55 6.37
3.73 3.33
2.50 2.49 2.47 2.46
1.18 1.17 1.06 1.04
OCOCF3
iPr
Au
N
Ph
OMe
5f
1H NMR (500 MHz), DMSO-d6
1.00 1.00 1.00 2.02 3.01 1.01 1.01 4.01 1.00 2.00 1.04 2.05 2.08 2.01
3.01
4.19
12.04 11.97
Chemical Shift (ppm)

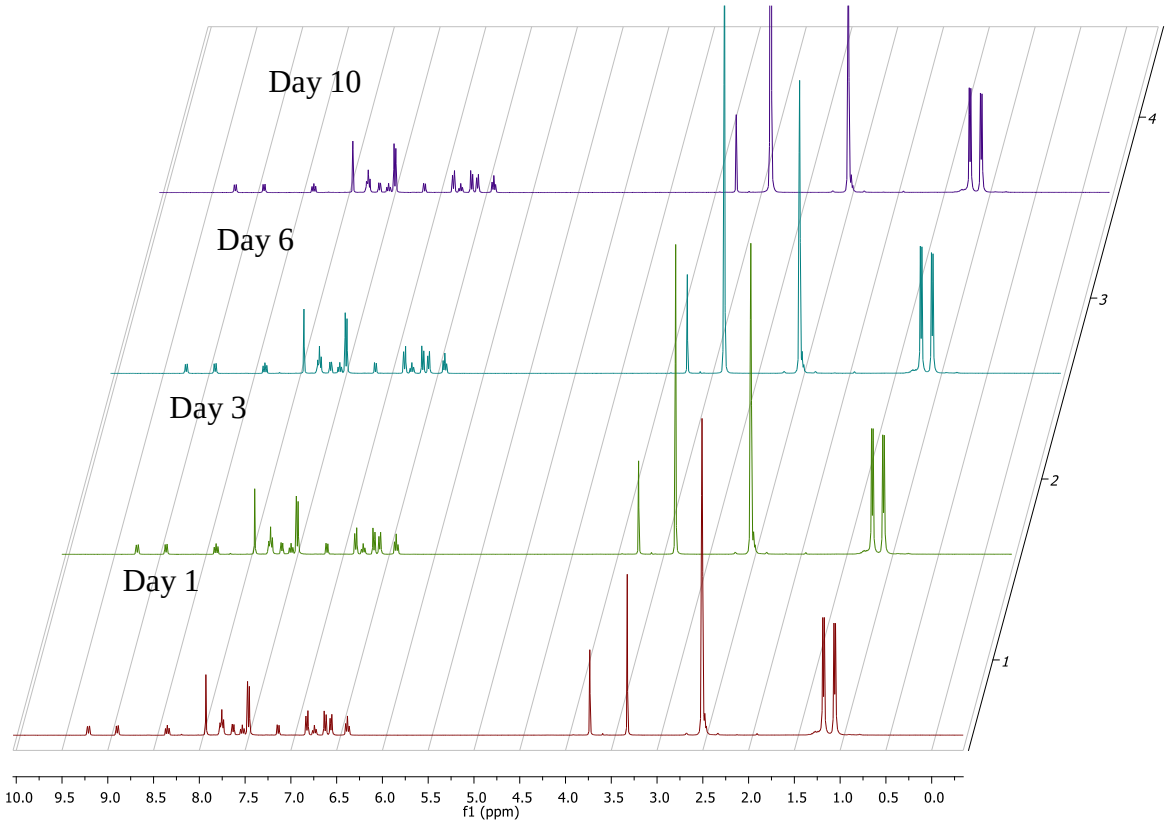

DMSO-d6
189.67
168.13 159.71 157.36 149.07 146.23 145.22 144.34 142.93 134.40 130.47 130.41 128.75 127.43 127.37 124.79 124.14 123.45 120.82 115.62 113.72
55.41 39.86 39.75 39.63 39.51 39.39 39.27 39.15 28.27 23.93 23.44
OCOCF3
iPr
Au
N
Ph
OMe
5f
13C NMR (175 MHz), DMSO-d6
Chemical Shift (ppm)

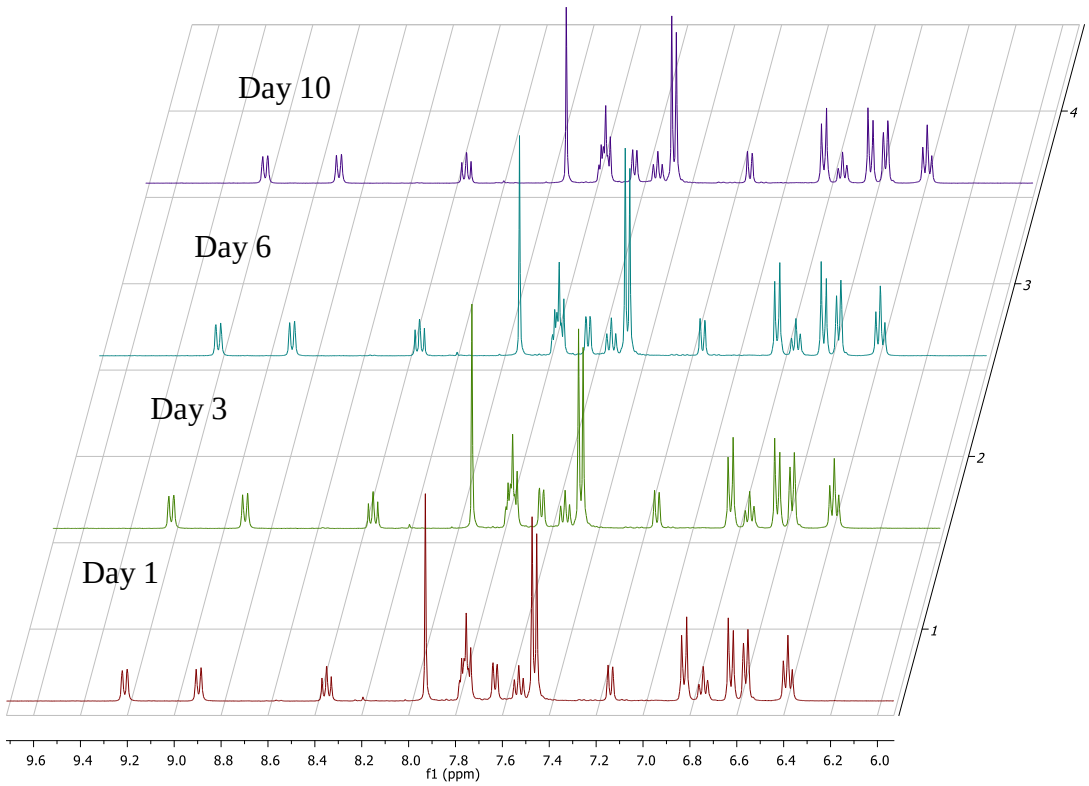
6 Stability studies of BQ-AurIPr

6.1. Stability for upto 10 days in DMSO

Stability of BQ-AurIPr in DMSO was analyzed by ^{1}H NMR in DMSO-D_6 over 10 days. As observed, no decomposition was detected upto 10 days.

Figure S6.1.1. Stability of BQ-AurIPr NMR in DMSO-d_6 over 10 days.



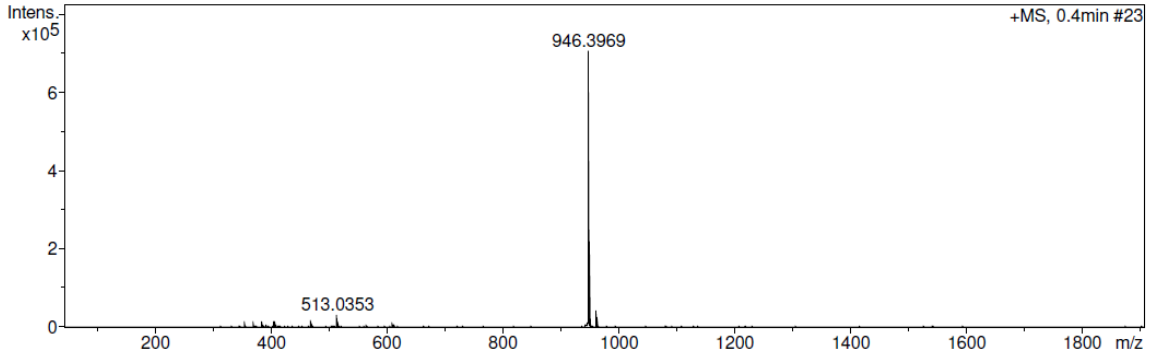


6.2 Stability in buffer solution:

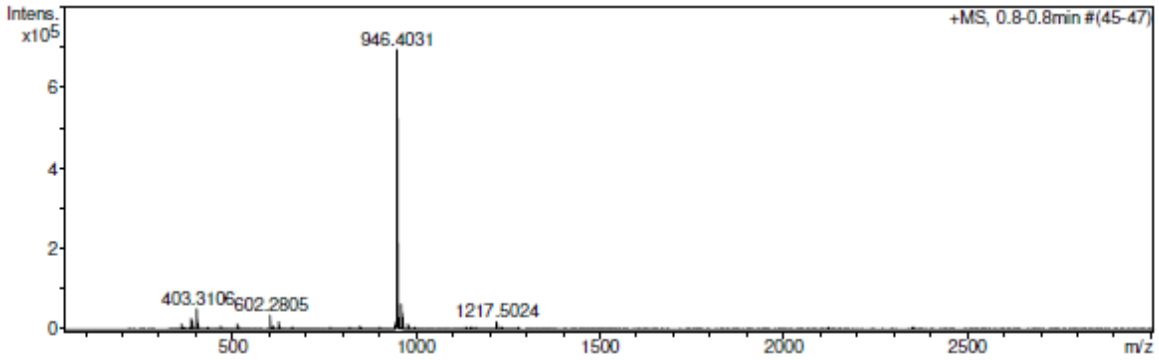
Mass spectrometry studies were performed to analyze the stability of BQ-AurIPr in buffer solutions. BQ-AurIPr was diluted in DMSO to prepare a solution of 5mM which was then further diluted to 5 µM in Ammonium Carbonate buffer (1M, pH 7.2). The reaction was incubated at 37 °C for given time. Samples were analyzed by direct infusion (DI) at a flow rate of 180 µL/h. Mass spectra were acquired and averaged over 1 min and processed using micrOTOF-Q II 10330. The instrumental parameters were as follows: 4.5 kV capillary voltage, 180 °C set dry hearter, temperature, <6 bar nebulizer pressure. Mass spectra once were acquired were processed using Bruker Compass Data Analysis 4.0 software.

Figure S6.2.1. Excerpts of the mass spectra of **BQ-AurIPr** incubated in ammonium carbonate (1M, pH = 7.4) for 24h.

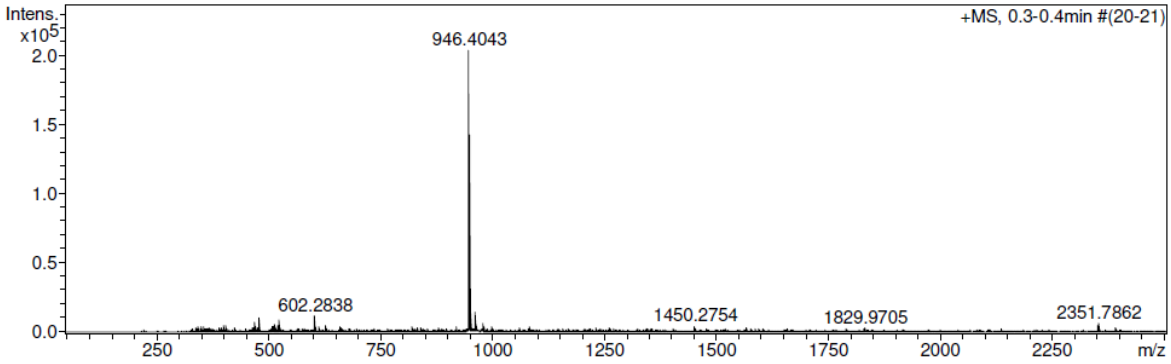
A) T = 0 hr



B) T = 4 hr



C) T = 24 hr



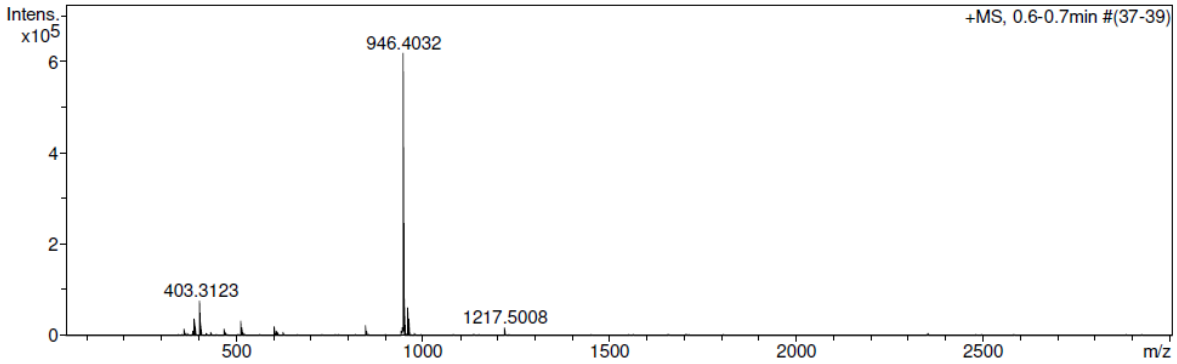
6.3 Reaction with glutathione:

BQ-AurIPr was diluted in DMSO to prepare a solution of 5mM which was then further diluted to 5 µM in Ammonium Carbonate buffer (1M, pH 7.2) and 5 equivalents of glutathione was added and the reaction was allowed to incubate for 24h. Aliquots of samples

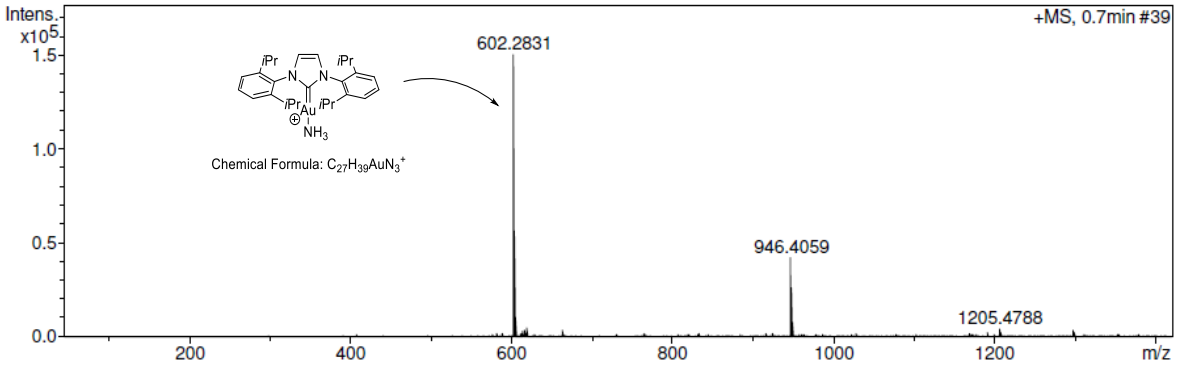
were collected and further diluted to 2.5uM with methanol and analyzed via mass spectrometry.

Figure S6.3.1. Excerpts of the mass spectra of **BQ-AurIPr** incubated with and without 5 equivalents glutathione in ammonium carbonate (1M, pH = 7.4) for 24h.

a) Without Glutathione, after 24h:

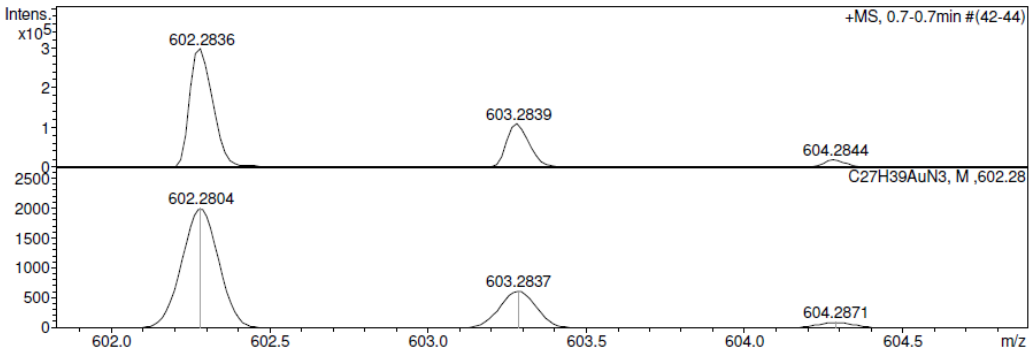


b) With 10 eq Glutathione, after 24h:



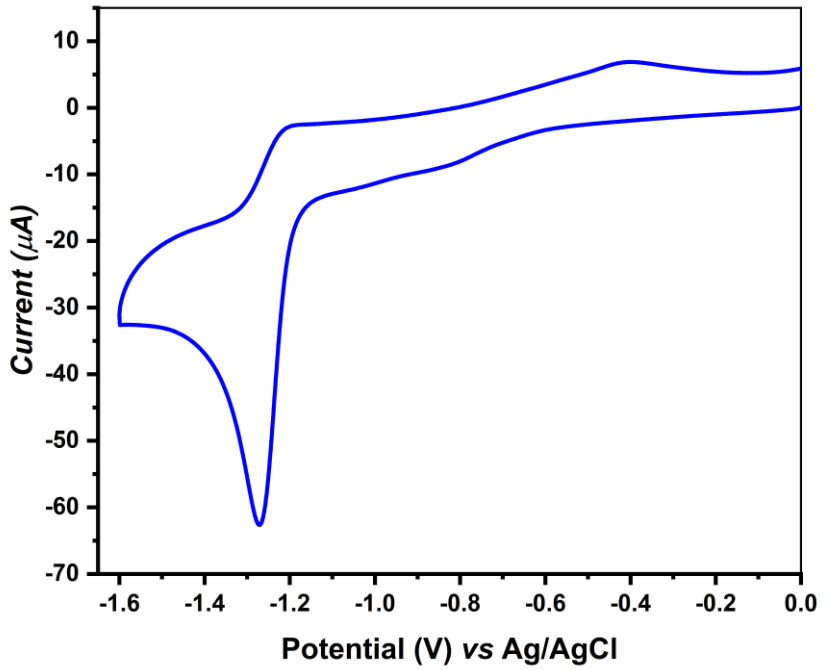
Reaction of glutathione with BQ-AurIPr in NH_4HCO_3 led to the formation of a new peak at 602.2831 which is proposed to be [IprAu(NH_3)] which was confirmed by HRMS data as follows; simulated mass spectrum has also been attached for comparison.

Figure S6.3.2. HRMS spectra of $[IPrAuNH_3]^+$. Simulated mass spectrum has also been attached for comparison



7 Electrochemical measurements

Electrochemical measurements were performed CHI700E biopotentiostat workstation using a Ag/AgCl (0.1M aq. KCl) as a reference electrode, a glassy carbon (GC) of 3.5 mm diameter (surface area = 0.07cm^2) working electrode and a Pt wire auxiliary electrode in a three-electrode cell under an argon atmosphere. The electrochemical measurements were performed using 1.0 mM solutions of the analyte in dry acetonitrile using ^{n}Bu$_4$NPF$_6$ (0.1 M) as the supporting electrolyte.



8 Biological studies

8.1 Screening of compounds

The focus of this study was to synthesize a potent anticancer compound which also has capacity to induce immunogenic cell death (ICD). Therefore, we synthesized compounds in several phases. After each phase of synthesis, we performed biological assays for determination of anticancer activity and ICD. Inferences from these biological assays were utilized to synthesize the next phase of compounds.

Cell viability analysis by MTT assay: Three different types of cell lines were used for analysis of anti-proliferation effect of synthesized molecules. A549 (lung carcinoma), Hela (cervical adenocarcinoma) and BHK-21 (normal) cells were maintained in T25 flasks (Corning) at 37 °C in the presence of 5% CO_2. A549 cells were cultured in F-12K media (Gibco) while Hela and BHK-21 cells were cultured in Dulbecco's Modified Eagle Medium (DMEM) media (Gibco) supplemented with 10% FBS (Gibco) and 1X antibiotic-antimycotic (Gibco). Cells were harvested and seeded into 96 well plates (Corning) at a density of 1500 cells/well and were allowed to incubate overnight. Stock solutions (50 μM) of synthesized chemical compounds were made by dissolving them in appropriate amount of DMSO. Next day, serial dilutions of stocks were made in culture media and from these 100 μL was added to each well of 96 well plates. Cells were incubated in presence of chemical compounds for 48 hours at 37 °C followed by incubation in 100 μL culture media containing 5 mg/ml of 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) for 3 hours. Media was aspirated and 50 μL of DMSO was added to each well, formazan absorbance was recorded at 560 nm using a microplate reader (Glomax multi plus detection system, Promega). Absorbance values were corrected for background and normalized to the well containing untreated cells. The data are shown as mean inhibition of growth as percentage of control cells (treated with 0.05% DMSO) and represents data from three separate experiments. IC_{50} values were calculated by regression analysis using Microsoft Excel software.

Analysis of ATP secretion by luciferase assay: A549 cells were seeded in a 6 well plate **(**$4x10^5$ cells per well) and cultured overnight. Cells were washed with PBS and treated with either vehicle or compounds (concentrations of compounds used was equivalent to IC50 value) for 4 hours. 200 μL of supernatant was collected from each well and centrifuged to

remove cells and debris. 50 µL of supernatant was added to a white opaque 96 well plate and relative amount of ATP was estimated using ATP determination kit according to manufacturer's instructions. Luminescence was measured using Glomax multi plus detection system (Promega).

Phase-1: The 17 BQ-AuPPh$_3$ complexes (*cf.* Section 4) were first subjected to MTT assay for cell viability studies in Hela cells. It was observed that **3c** (IC_{50} value = ~4.7 µM), **3i** (IC_{50} value = ~5.6) and **3k** (IC_{50} value = ~3.4) performed well among the 17 compounds tested and were studied next for their ATP secretion. **3c** was found to be most effective in comparison to **3i** and **3k**, and hence BQ core as in **3c** was carried forward to next phase where the ligands on gold complexes were screened.

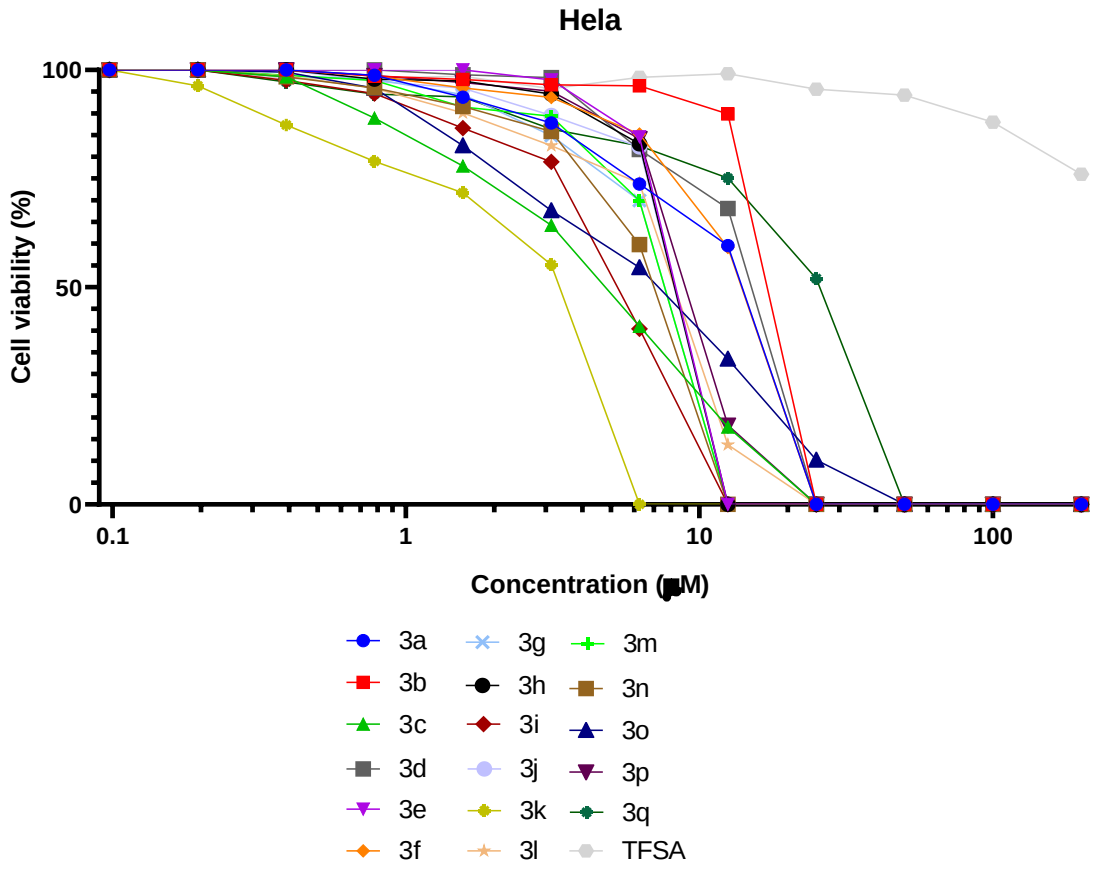


Figure S8.1.1. Cell viability analysis of Hela cells after treatment with compounds synthesized in phase-1.

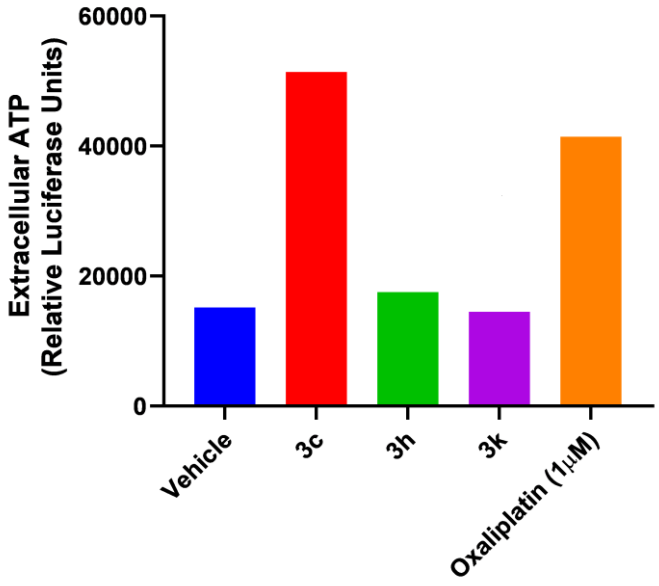


Figure S8.1.2. Analysis of ATP secretion by Hela cells when treated with IC50 concentration of compounds synthesized in phase-1.

Phase II: With the best BQ substitution being identified, variation on the other ligand on gold complex was studied (*cf.* Section 4). In this regard, we synthesized various phosphine and NHC-based complexes of BQ-AuL. These complexes were subjected to MTT and ATP secretion assays for viability and ICD, respectively. The results suggest that **4k** performed exceptionally well in comparison to other compounds in the group.

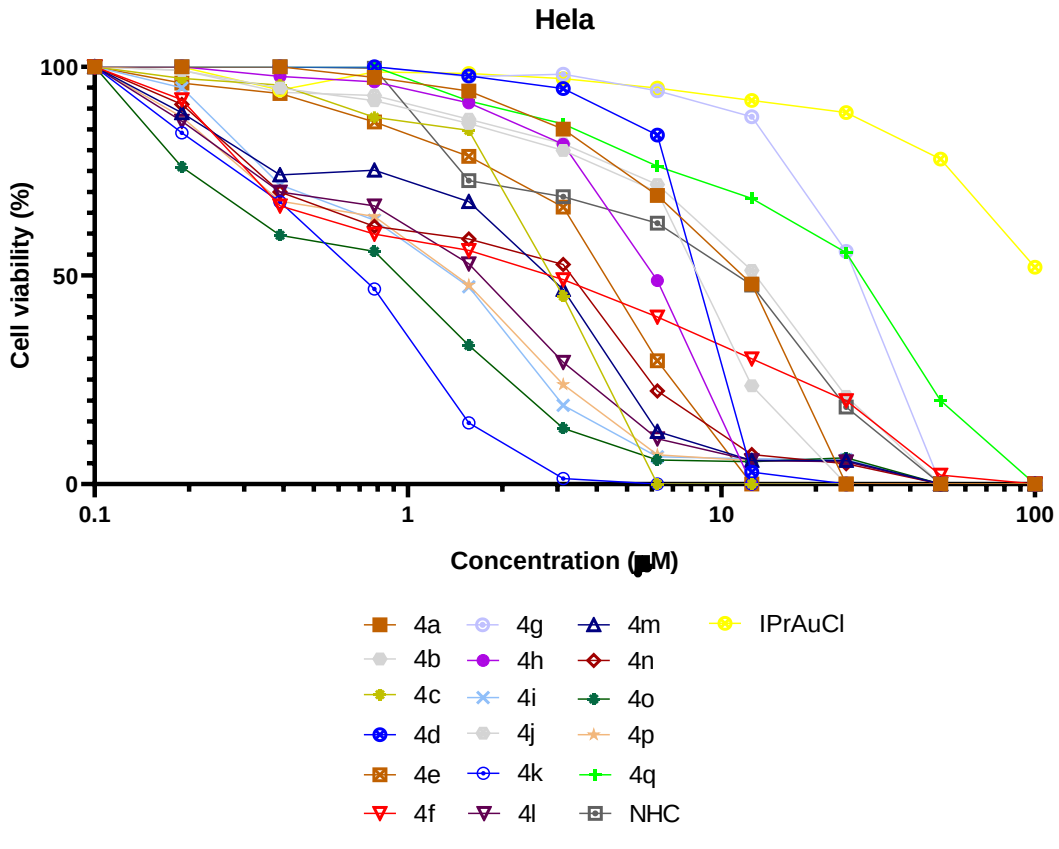


Figure S8.1.3. Cell viability analysis of Hela cells after treatment with compounds synthesized in phase-2.

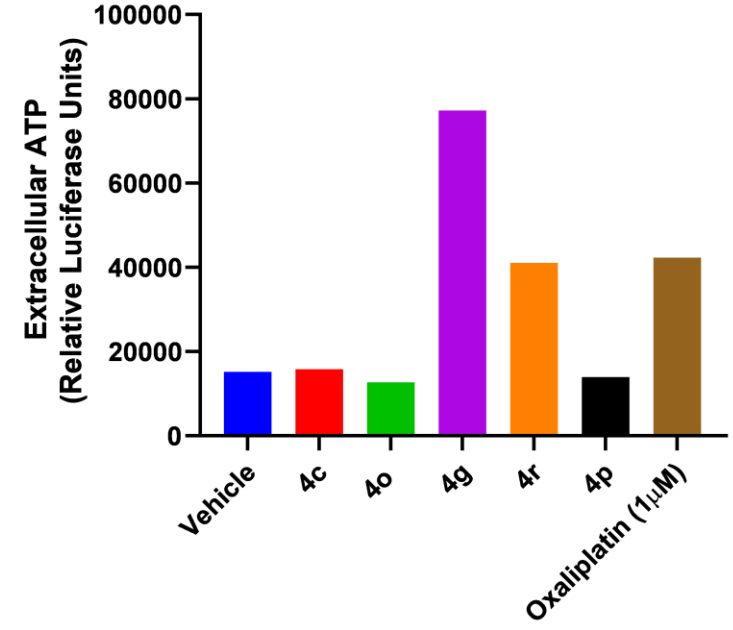


Figure S8.1.4. Analysis of ATP secretion by Hela cells when treated with IC50 concentration of compounds synthesized in phase-2.

<u>Phase III</u>: Two other potent combination with IPr as ligand in BQ-AuL and five other variants of **4k** bearing different counter-anions (**5a-5f**) were screened. **4k** was found to be best in terms of IC_{50} and ATP secretion as can be seen below.

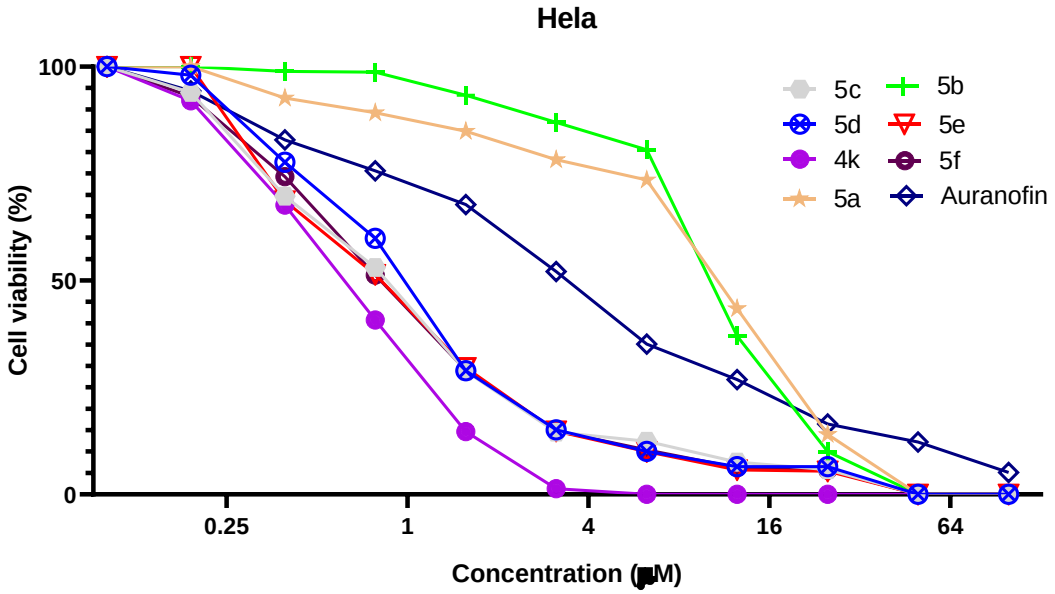
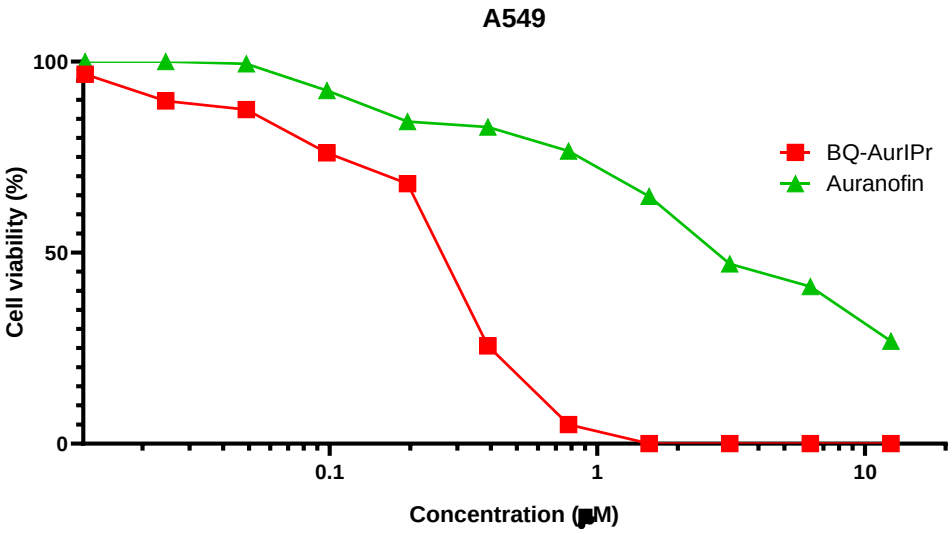
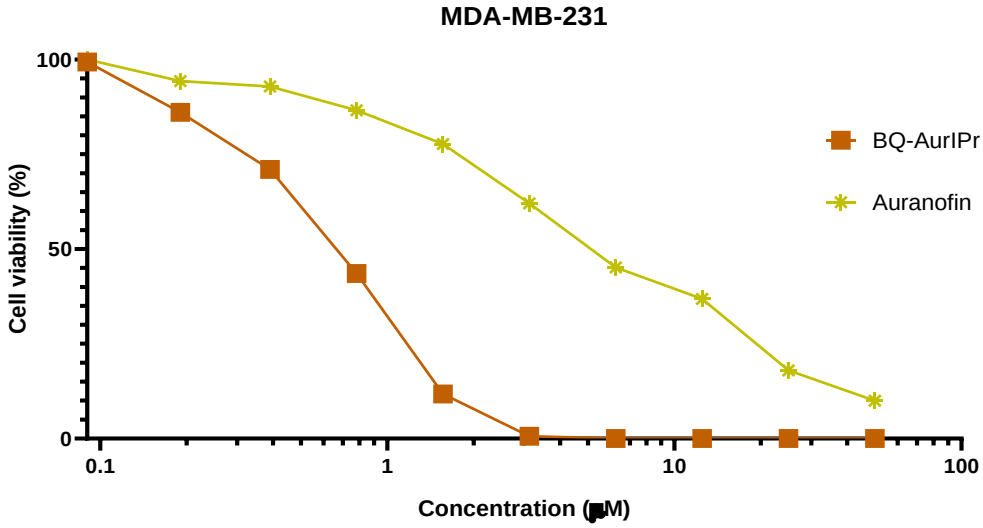


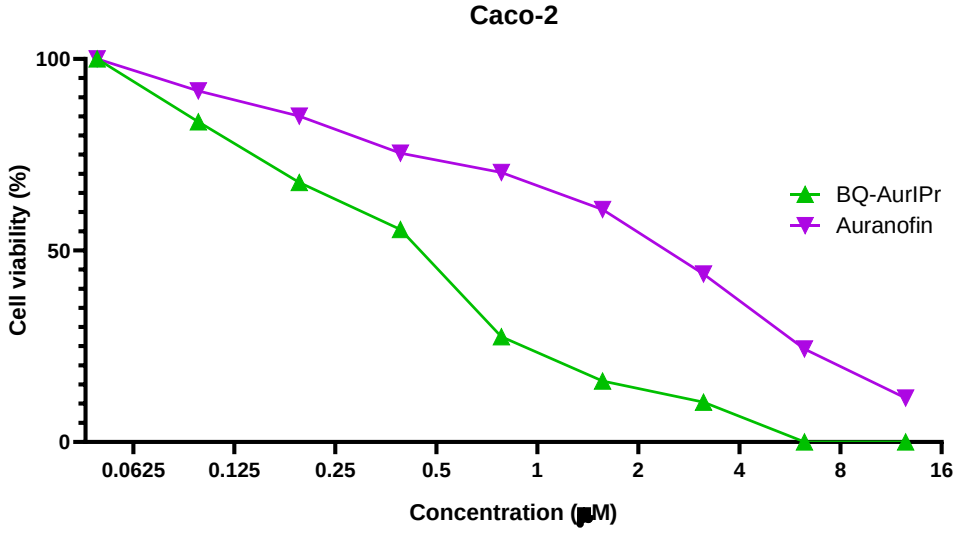
Figure S8.1.5. Cell viability analysis by MTT assay of compounds synthesized in phase-3.

8.2 Analysis of anticancer activity

After identification of the lead compound (**4k**) referred henceforth as '**BQ-AurIPr**', we tested its anticancer activity in different types of cancer cells and normal human cells. Non-small cell lung cancer cells (A549), colorectal adenocarcinoma (Caco-2), and breast cancer (MDA-MB-231), and primary human small airway epithelial cells (hSAEC) were used for this study. IC50 value of BQ-AurIPr in primary normal hSAECs was used for calculation of selectivity index in cancer cells.


A549
100
50
0
Cell viability (%)
0.1
1
10
Concentration (μM)
BQ-AurIPr
Auranofin


MDA-MB-231
100
50
0
Cell viability (%)
0.1
1
10
100
Concentration (μM)
BQ-AurIPr
Auranofin


Caco-2
100
50
0
Cell viability (%)
0.0625
0.125
0.25
0.5
1
2
4
8
16
Concentration (μM)
BQ-AurIPr
Auranofin

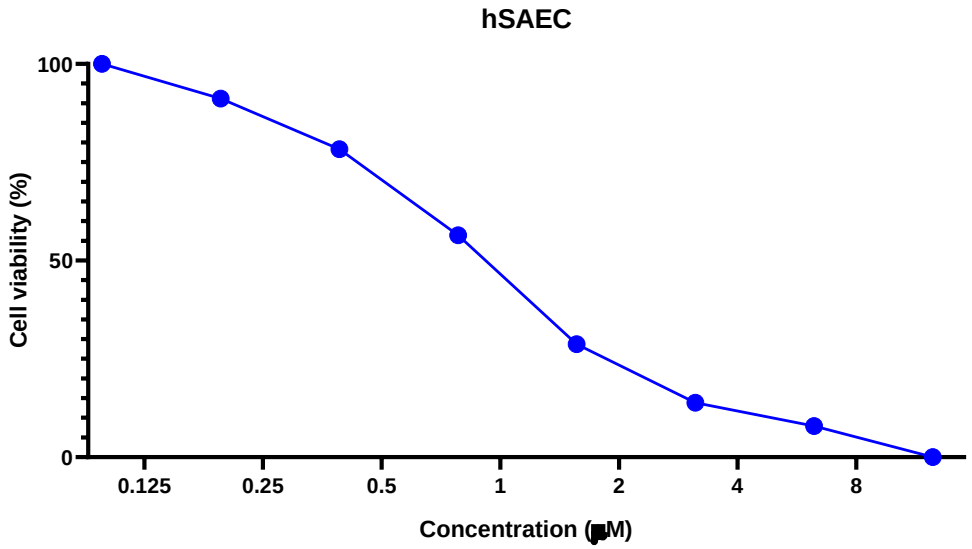


Figure S8.2.1. Cell viability analysis of different types of cancer cells after treatment with BQ-AurIPr by MTT assay.

8.3 **Cell migration and invasion assay**

Cancer cells have three characteristics that make them different from normal body cells and help them cause the disease. These characteristics are-

- Cancer cells proliferate at much higher rate than normal body cells.
- Unlike normal body cells cancer cells can migrate to their immediate surroundings.
- Cancer cells secrete proteases that digest the extracellular matrix enabling them to invade distant organs (metastasis).

Till now we have analysed only one aspect of anticancer activity, that is anti-proliferative effects of BQ-AurIPr. Next, we analysed other two aspects by cell migration and invasion assays. BQ-AurIPr showed highest anticancer activity in A549 cells. Therefore, we focused our study on A549 cells.

a) Cell migration analysis: A549 cells were seeded in 6 well plates at a density of $5x10^6$ cells/cm^2 and were incubated overnight in DMEM medium supplemented with 10% FBS (Gibco) and 1X antibiotic-antimycotic (Gibco). After overnight incubation cell monolayer was

scratched using a 200 µL pipette tip to introduce a wound, suspended cells were washed twice with PBS and wounded monolayer of cells was incubated in serum free DMEM containing different concentrations of BQ-AurIPr. Images of the wound were captured at different time points using Axio Vert.A1 microscope (ZEISS) fitted with Jenoptik ProgRes MF Cool CCD camera. Areas of the wound were quantified using ImageJ 1.53h software (Media Cybernetics, Inc., USA). Experiment was carried out in triplicate and size of the wound was plotted against time using GraphPad prism.

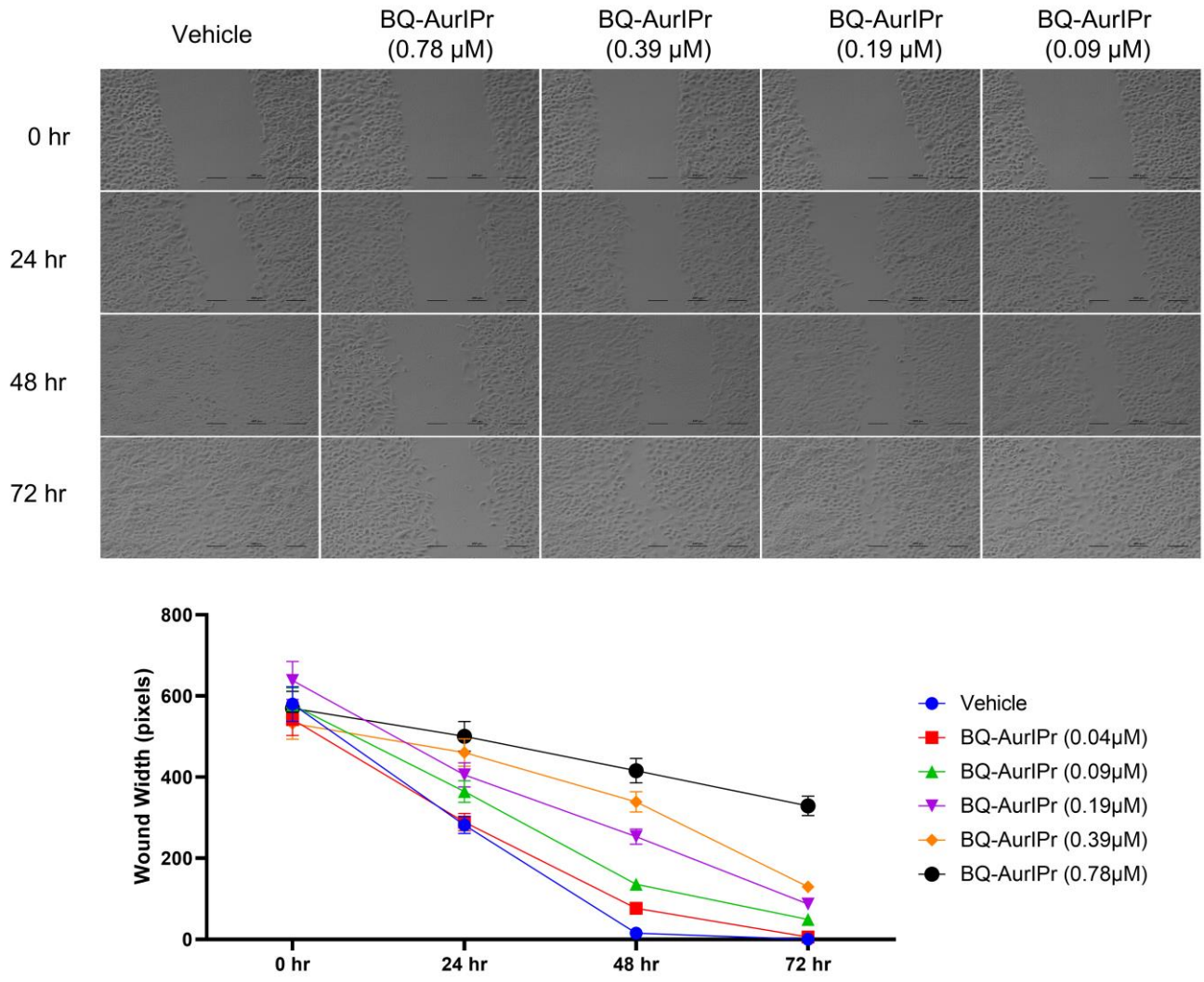


Figure S8.3.1. Analysis of anticancer activity of BQ-AurIPr by Cell migration assay in A549 cells.

b) Cell invasion analysis: A transwell culture system was used for analysis of cell invasion potential of cancer cells; it is composed of two chambers separated by a porous membrane. Cell culture inserts (Falcon, Becton Dickinson, USA) with pore size 8 µm were coated with 50 µL ECM Gel from Engelbreth-Holm-Swarm murine sarcoma (E1270, Sigma-Aldrich) and were left for overnight air drying and polymerization in a laminar flow hood. ECM gel was blocked using 2% BSA a at 37 °C for 2 hours followed by washing with PBS. $2x10^4$ A549 cells were placed on upper layer of transwell chamber, cells were either exposed to 0.25 µM BQ-AurIPr or Vehicle for 4 hours. Lower chamber was filled with medium containing 10% FBS as a chemotactic agent. After incubation at 37 °C for 24 hours, cells remaining in the upper chamber were removed using cotton swabs. Cells that crossed the membrane and adhered to the lower side of membrane were fixed with methanol and stained with 0.1% crystal violet for 10 minutes. Membrane was rinsed thoroughly in PBS and was mounted onto a glass slide after detaching from insert. Images of 5 different fields were taken using an Olympus CKX41 microscope and a digital colour camera and number of cells per field of view were plotted using GraphPad Prism.

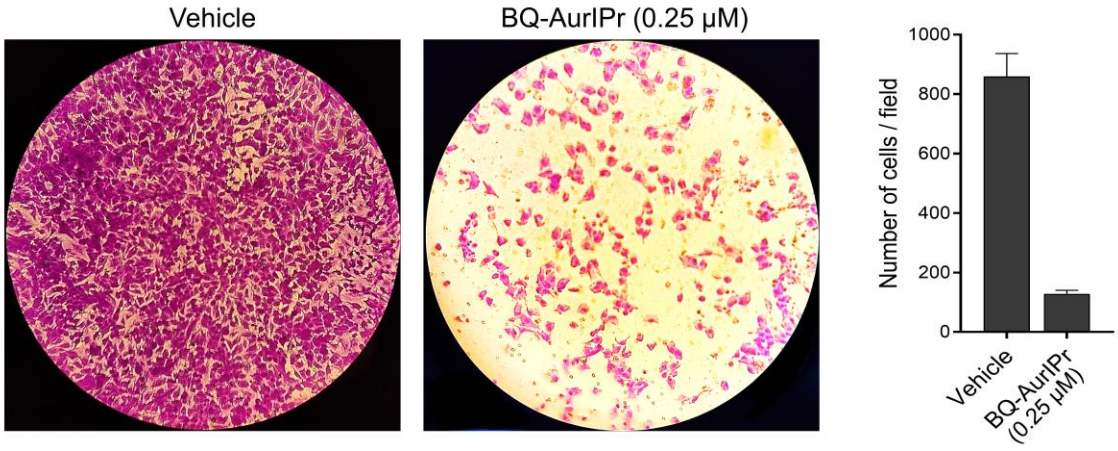


Figure S8.3.2. Analysis of anticancer activity of BQ-AurIPr by Matrigel invasion assay in A549 cells.

8.4 Detection of reactive oxygen species (ROS) generation

For analysis of ROS generation, we employed a cell-permeant ROS indicator 2',7'-dichlorodihydrofluorescein diacetate (H2DCFDA). After H2DCFDA treatment cells were analysed using two separate methods confocal microscopy and flow cytometry.

ROS detection by confocal microscopy: A549 cells were grown on glass cover slips in a 6 well plate at a seeding density of $3x10^5$ per well and cultured overnight at 37 °C in a 5% CO_2 incubator. Cells were either treated with vehicle or different concentrations of BQ-AurIPr for 4 hours at 37 °C in a CO_2 incubator. Cells were washed in PBS and incubated with 1 μM H2DCFDA in PBS for 15 minutes at 37 °C. Cells were washed twice with PBS and incubated with 50nM Mitotracker® Red CMXRos solution (made in PBS) for 20 minutes at 37 °C. After incubation cells were washed twice with PBS and were fixed with 4% paraformaldehyde solution for 10 minutes. After fixation cells were washed twice with PBS and incubated with DAPI staining solution (300 nM) for 5 minutes. Post DAPI staining cells were washed thrice with PBS and the coverslip was mounted onto a glass slide with the help of Fluoroshield™ mounting media (Sigma-Aldrich). Slides were visualized using a 63X objective lens on Live cell confocal microscope (Zeiss).

ROS detection by flow cytometry: Cells were seeded at a density $3x\ 10^5$ per well in a 6 well plate and cultured overnight 37 °C in a 5% CO_2 incubator. Cells were either treated with vehicle or different concentrations of BQ-AurIPr for 4 hours at 37 °C in a CO_2 incubator. Cells were washed in PBS and incubated with 1 μM H2DCFDA in PBS for 15 minutes at 37 °C. Cells were washed twice with PBS and incubated with 50nM Mitotracker® Red CMXRos solution (made in PBS) for 20 minutes at 37 °C. After incubation cells were washed with PBS and were detached using 1X trypsin-EDTA solution. Cell pellet was washed with PBS and fixed with 4% paraformaldehyde solution for 10 minutes. After fixation cell pellet was washed with PBS and dissolved in 1 ml of PBS for flow cytometric analysis on a FACS Aria-II flow cytometer (Becton Dickinson, USA). Data was analysed and processed using FlowJo v10 software (Becton Dickinson, USA).

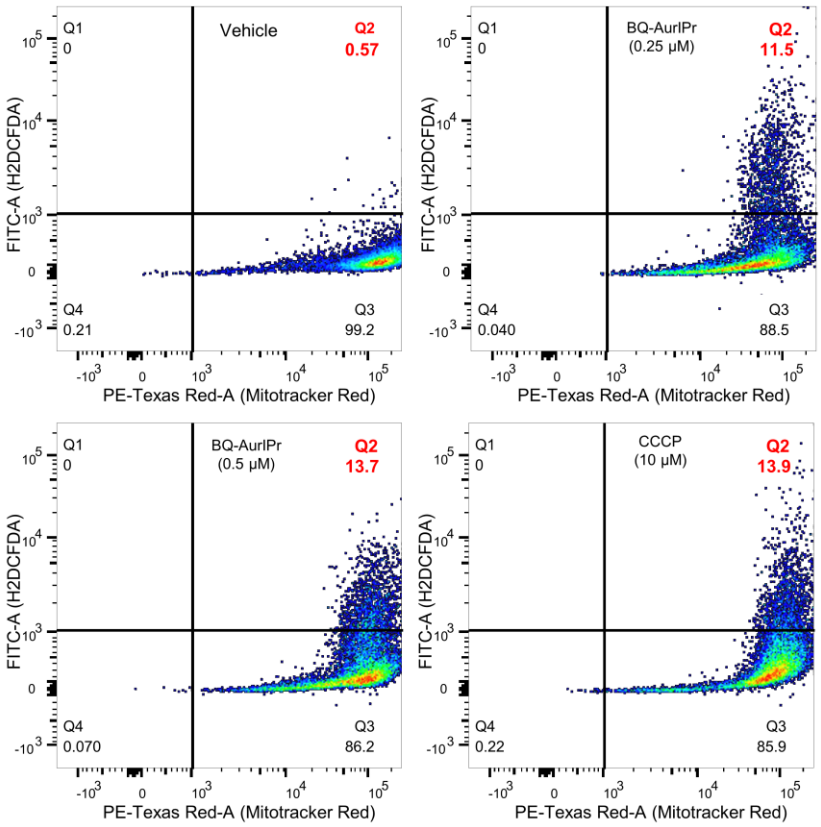


Figure S8.4.1. Analysis of ROS generation by BQ-AurIP in A549 cells.

8.5 **Cell cycle analysis and detection of apoptosis by flow cytometry**

Cells were seeded at a density $3x10^5$ per well in a 6 well plate and cultured overnight 37 °C in a 5% CO_2. Cells were washed and incubated with vehicle or different concentrations of BQ-AurIPr for 4 hours. After incubation cells were washed with PBS and cells were detached using 1X trypsin-EDTA. Cells were pelleted and pellet was washed twice with cold PBS. Cells were stained with fluorescent conjugate of Annexin-V and propidium iodide (PI) for 15 minutes and were diluted in binding buffer according to manufacturer's instruction (Invitrogen V13242). Samples were analysed using FACS Aria-II flow cytometer (Becton Dickinson, USA). Data was analysed and processed using FlowJo v10 software (Becton Dickinson, USA).

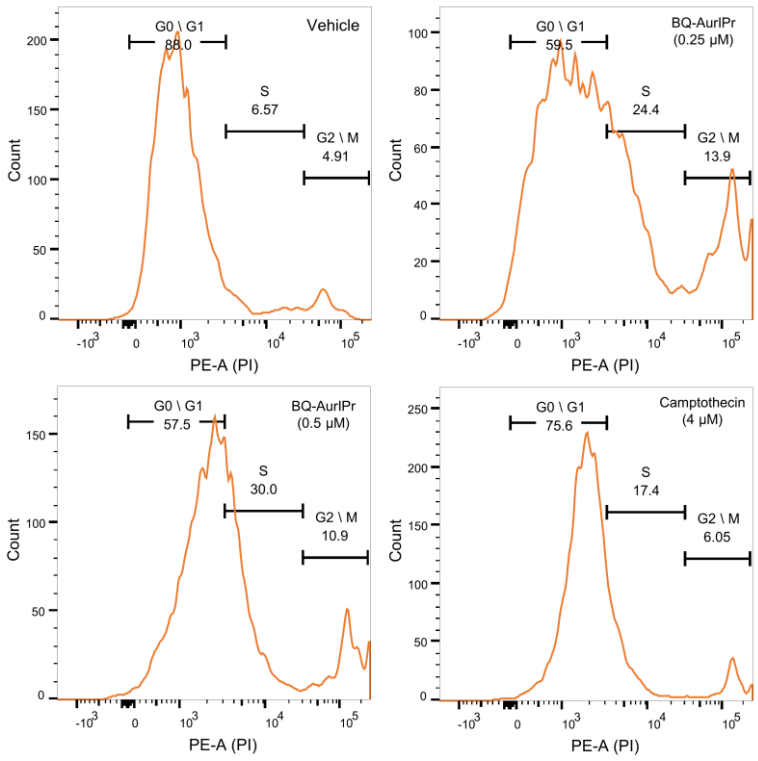


Figure S8.5.1. Cell cycle analysis of A549 cells after BQ-AurIPr treatment using propidium iodide.

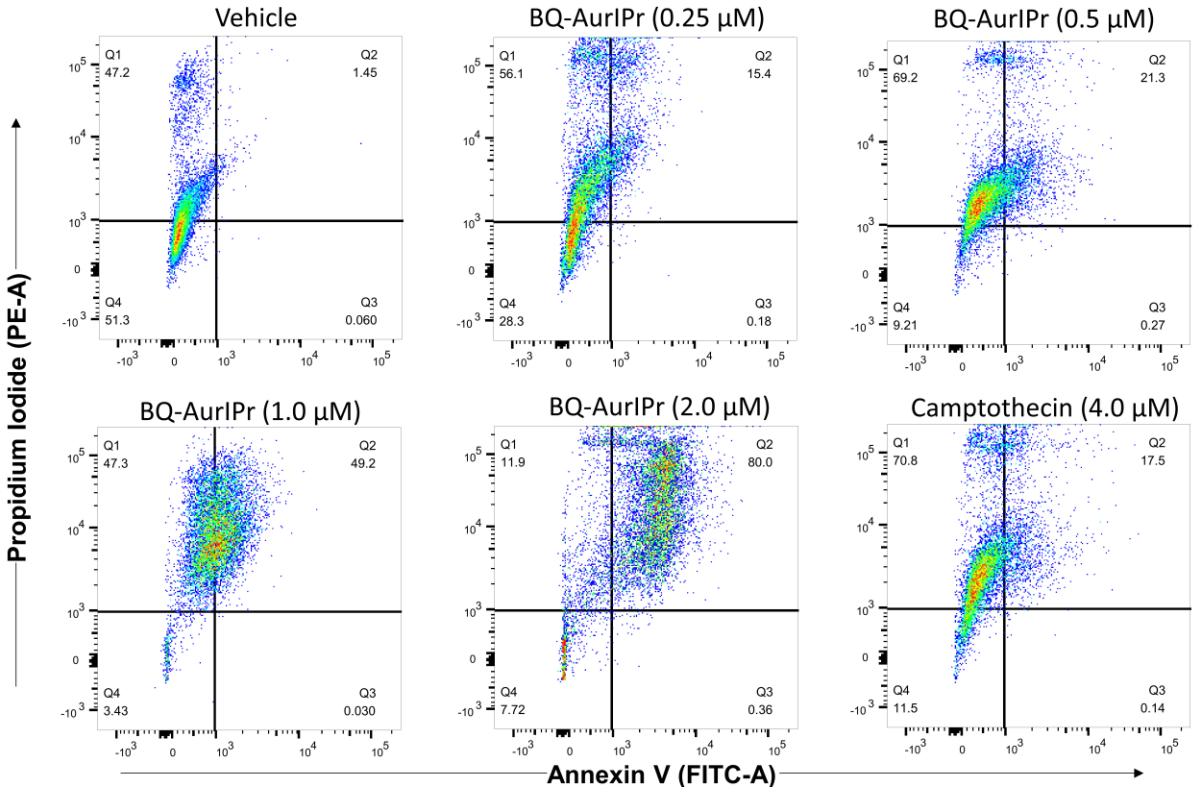


Figure S8.5.2. Analysis of induction of apoptosis in A549 cells after BQ-AurIPr treatment using annexin V and propidium iodide staining.

8.6 **Confocal microscopy for calreticulin translocation**

Cells were harvested and cultured overnight on a glass cover slip in a 6 well plate at a seeding density of $2x10^5$ per well. Cells were washed with PBS and incubated either with vehicle or different concentrations of BQ-AurIPr for 4 hours at 37 °C. For staining cytoplasmic compartment cells were incubated with 50nM Mitotracker® Red CMXRos solution (made in PBS) for 20 minutes at 37 °C. Cells were washed twice with PBS and fixed with 4% paraformaldehyde for 10 minutes. After fixation cells were washed twice with PBS and non-specific epitopes were blocked with 1% BSA, 22.52 mg/mL glycine in PBS for 30 min. Cells were washed with PBST and incubated with anti-calreticulin antibody (1:150 dilution made in PBST containing 1% BSA) for 1 hour at room temperature in a humidified chamber. Cells were washed twice with PBS and incubated with secondary anti-mouse alexa fluor 488 antibody (1:500 dilution made in PBST containing 1% BSA) for 45 minutes at room temperature in a humidified chamber. Cells were washed thrice with PBST and stained with DAPI (300 nM) for 5 minutes. Post DAPI staining cells were washed thrice with PBST and the coverslip was mounted onto a glass slide with the help of Fluoroshield™ mounting media (Sigma-Aldrich). Slides were visualized under 63X objective lens using Olympus laser scanning confocal microscope (LSM-700).

8.7 **Detection of HMGB1 by ELISA**

A549 cells were seeded in a 6 well plate **(**$4x10^5$ cells per well) and cultured overnight. Cells were washed with PBS and treated with either vehicle or different concentrations of BQ-AurIPr or doxorubicin (20 μM) for 4 hours. 200 μL of supernatant was collected from each well and centrifuged to remove cells and debris. To estimate HMGB1 concentration serial two-fold dilutions of standard were made (ranging from concentrations 5000 pg/ml to 78 pg/ml). 100 μL of standard or sample supernatant was added to respective wells and assay was conducted according to manufacturer's instructions (Cusabio, CBS-E08223h). Absorbance was recorded at 450 nm and 570nm and 570 absorbance was subtracted from 450 absorbance. A standard curve was made by plotting known standard concentrations against

absorbance and concentration of HMGB1 in samples was calculated through regression analysis.

8.8 **Analysis of mitophagy**

A549 cells were seeded in a 6 well plate **(**$4x10^5$ cells per well) and cultured overnight. Cells were washed with PBS and treated with either vehicle or different concentrations of BQ-AurIPr or doxorubicin (20 μM) for 12 hours. After 12 hours cells were analysed for mitophagy using Real time polymerase chain reaction (RT-PCR), flow cytometry or confocal microscopy.

RT-PCR analysis: For analysis of RNA expression of mitophagy related genes supernatant was removed and cell monolayer was washed and lysed in Trizol reagent (Invitrogen). RNA was isolated following manufacturer's instructions. 1 μg of RNA was used to prepare cDNA using iScript cDNA synthesis kit (BIO-RAD). RT PCR was performed using KAPA SYBR FAST qPCR mastermix and 1μl of cDNA as sample on an Applied Biosystems StepOnePlus real time PCR system. Gene expression relative to 18s rRNA was analysed using StepOne software v 2.2.2.

Flow cytometry: For analysis of mitophagy by flow cytometry cells were washed twice with PBS and incubated with 50nM Mitotracker® Red CMXRos solution (made in PBS) for 20 minutes at 37 °C. After incubation cells were washed with PBS and were detached using 1X trypsin-EDTA solution. Cell pellet was washed with PBS and fixed with 4% paraformaldehyde solution for 10 minutes. After fixation cell pellet was washed with PBS and dissolved in 1 ml of PBS for flow cytometric analysis on a FACS Aria-II flow cytometer (Becton Dickinson, USA). Data was analysed and processed using FlowJo v10 software (Becton Dickinson, USA).

Confocal microscopy: For analysis of mitophagy by confocal microscopy, cells weregrown on glass coverslips. After 12 hour treatment cells were washed with PBS and incubated with 50nM Mitotracker® Red CMXRos solution (made in PBS supplemented with 0.1% BSA) for 20 minutes at 37 °C. After incubation cells were washed thrice with PBS and were incubated with 50nM Lysotracker DND-22 solution (made in PBS supplemented with 0.1% BSA). Cells were washed thrice with PBS and fixed with 4% paraformaldehyde solution for 10 minutes. After fixation cells were washed twice with PBS and the coverslip was mounted onto a glass

slide with the help of Fluoroshield™ mounting media (Sigma-Aldrich). Slides were visualized under 63X objective lens using Olympus laser scanning confocal microscope.

8.9 **Isolation of peripheral blood mononuclear cells (PBMCs)**

10 ml blood was drawn from a healthy voluntary donor by venipuncture of median cubital vein, the procedure was done by a trained health personnel. Blood was collected in vacutainer tubes containing anticoagulant. Anticoagulated blood was layered onto equal volume of Histopaque-1077 (Sigma Aldrich) in a 15 ml conical tube and centrifuged at 400 x g for 30 minutes at room temperature. After centrifugation upper layer was discarded and the opaque interface containing mononuclear cells were collected in a clean 15 ml centrifuge tube. Cells were washed twice with 10 ml of RPMI media and cell pellet was collected by centrifuging at 250 x g for 10 minutes. Final cell pellet was dissolved in 2 ml of RPMI medium containing 10% FBS and 1X antibiotic-antimycotic. Cells were counted under a light microscope using a Neubauer chamber and diluted accordingly for further experiment requirements.

8.10 **In-vitro analysis of Immunological cell death**

Cells undergoing apoptosis after treatment with BQ-AurIPr express damage associated molecular patterns or DAMPs (ATP, HMGB1, calreticulin, etc.). To analyse if these DAMPs are actually able to induce immune cells, we employed an indirect cell co-culture method composed of two compartments separated by a porous membrane (Boyden chamber). As a model for human immune system, we used peripheral blood mononuclear cells (PBMCs) isolated from healthy donors. These immune cells were co-cultured with tumor cells (A549) pre-treated with BQ-AurIPr for 4 hours. After 4 hours upper chamber containing tumor cells was removed and supernatant from lower chamber was analysed for cytokines (IL-6, TNF-α, IL-1β, and IP-10) indicative of immune system activation by ELISA (Becton Dickinson, USA).

8.11 **Phagocytosis Assay**

For differentiation THP-1 cells were cultured in complete RPMI media supplemented with 30nM phorbol myristic acetate phorbol 12-myristate-13-acetate (PMA) for 48 hours followed by another 48 hours culture in complete RPMI media without PMA. Cells were labelled with CellTracker™ Red dye and detached using a cell scraper. For performing phagocytosis assay

green fluorescence protein expressing A549 cancer cells were either treated with 0.25 µM BQ-AurIPr or vehicle for 6 hours. A549 cells were scraped using cell scraper and were co-cultured with labelled THP-1 cells for 2 hours at 37 °C in CO_2 incubator. After incubation cells were fixed with 4% paraformaldehyde and analysed using FACS Aria-II flow cytometer (Becton Dickinson, USA). Data was analysed and processed using FlowJo v10 software (Becton Dickinson, USA).