

Supporting Information for

**Synthesis of Azulenyl-Substituted Gold(I)-Carbene Complexes and Investigation of their
Anticancer Activity**

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List of Abbreviations

ATR	Attenuated Total Reflectance
Calcd.	Calculated
DCM	Dichloromethane
EA	Ethyl Acetate
HR-MS	High Resolution Mass Spectrometry
IR	Infrared Spectroscopy
<i>J</i>	Scalar coupling
K	Kelvin
MALDI	Matrix-Assisted Laser Desorption /Ionization
MHz	Megahertz
MP	Melting Point
NMR	Nuclear Magnetic Resonance
PE	Petroleum Ether
r.t.	Room Temperature
UV-Vis	Ultraviolet-Visible Spectroscopy

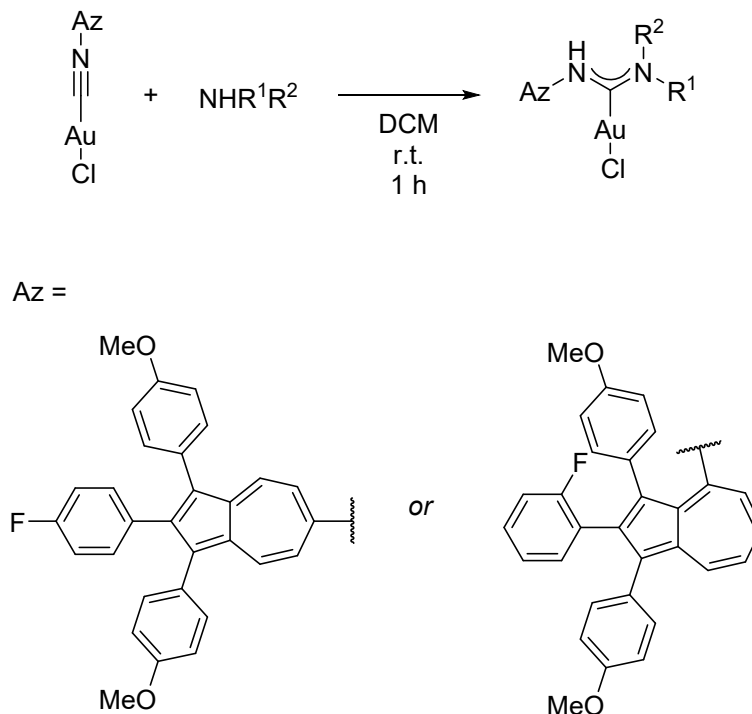
1 General Remarks

All chemicals and solvents were purchased from the commercial suppliers ABCR, BLDPharm, Chempur, Fluorochem, TCI or Sigma-Aldrich. All purchased substances were used without prior purification. Deuterated solvents were purchased at Deutero, Eurisotop or Sigma-Aldrich. Absolute reagent grade solvents were filled in Schlenk flasks under nitrogen atmosphere from the solvent purification system MB-SPS-800 Benchtop or purchased from the aforementioned commercial suppliers. Reactions under inert conditions were conducted in flame-dried Schlenk flasks under nitrogen atmosphere. Analytical thin layer chromatography was performed on precoated Macherey-Nagel POLYGRAM® SIL G/UV254 or Merck TLC Silica gel Gel 60 F254 aluminium TLC plates. Flash column chromatography was performed using silica gel (0.04 – 0.063 mm / 230 – 400 mesh ASTM) obtained from Macherey-Nagel as a stationary phase. Solvent mixtures of petroleum ether (PE), ethyl acetate, dichloromethane (DCM) or Methanol (MeOH) were used as mobile phases. Melting points were measured with a BÜCHI B-540 melting point apparatus. NMR spectra were obtained at the spectrometers Bruker Avance III 300, Bruker Fourier 300, Bruker Avance DRX 300, Bruker Avance III 400, Bruker Avance III 500, Bruker Avance III 600 and Bruker Avance Neo 700. All chemical shifts δ are given in parts per million (ppm) and coupling constants J are given in Hertz (Hz). ^1H , and ^{13}C NMR spectra were calibrated relatively to residual solvent signals, such as CDCl_3 (7.26 ppm, 77.16 ppm), CD_2Cl_2 (5.32 ppm, 53.84 ppm), or C_6D_6 (δ 7.16 ppm, 128.06 ppm). The following abbreviations were used to indicate multiplicities in the ^1H NMR spectra: s (singlet), d (doublet), t(triplet), q (quartet), m (multiplet). The following abbreviations were used to indicate multiplicities in the ^{13}C NMR spectra: s (quaternary carbon atom, CR_4), d (tertiary carbon atom, CHR_3), t (secondary carbon atom, CH_2R_2), q (primary carbon atom CH_3R). Multiplicities were determined by ^{13}C DEPT and 2D ^1H , ^{13}C NMR experiments. All ^{13}C NMR Spectra were recorded with decoupling of the ^1H and ^{19}F nucleus All ^{19}F NMR spectra were recorded with decoupling of the ^1H nucleus. All raw data was processed using the software MestReNova 14.3. Infrared spectra were obtained from a FT-IR Bruker LUMOS with a Germanium ATR crystal. Mass spectra were measured at the MS facility of chemistry department of Heidelberg University. Electron Ionization (EI) spectra were measured on a JEOL JMS-700 or on a JEOL AccuTOF GCx spectrometer. Matrix-assisted laser desorption/ionization (MALDI) spectra were obtained from a Bruker ApexQe FT-ICR-MS or from a Bruker Autoflex Speed time-of-flight spectrometer. UV/Vis spectra were recorded on a JASCO V-670 spectrophotometer in the specified solvents. Single-crystal XRD analyses were performed at the chemistry department of Heidelberg University. The XRD data was collected

from a Stoe Stradivari with a Cu-microsource and Pilatus detector or from a BRUKER APEX II Quazar with a Mo-microsource. Single crystal structures were processed using the software Mercury 3.10.3. Cyclic voltammograms were measured on a VERSASTAT3-200 potentiostat with a glassy carbon working electrode, a silver reference electrode and a platinum coated titanium counter electrode. All measurements were performed in a 0.1M Solution of tetrabutylammonium hexafluorophosphate in degassed dichloromethane with ferrocene as an internal standard.

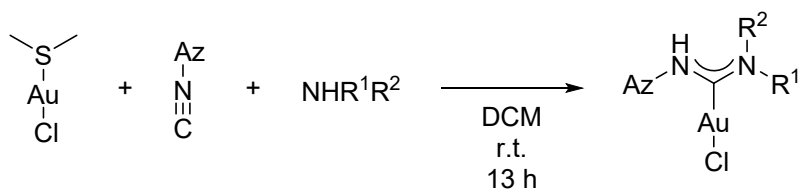
2 Synthesis of Compounds

2.1 General Procedure for the Synthesis of Azulene-tethered Carbene Gold(I) Complexes from Isonitrile Gold(I) Complexes (GP1)

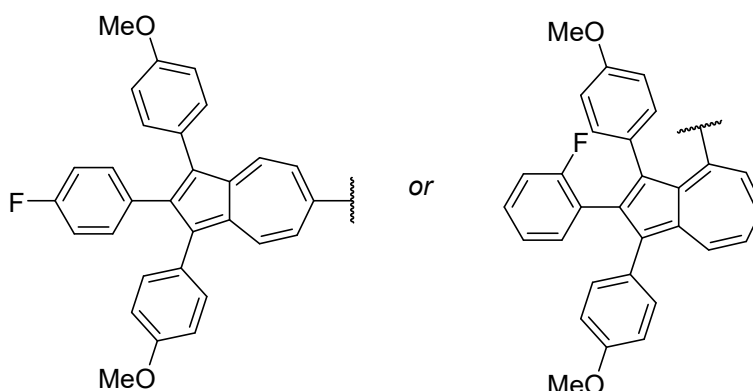


In a round bottom flask, the isonitrile gold(I) complex (1.00 eq.) was dissolved in reagent grade dichloromethane. Afterwards the appropriate amine (1.00 eq.) was added to the reaction mixture which was then stirred upon full consumption of the starting material. The crude reaction mixture was purified by flash column chromatography to obtain the corresponding azulene-tethered carbene gold(I) complex.

2.2 General Procedure for the One-Pot Synthesis of Azulene-tethered Carbene Gold(I) Complexes from [AuCl(DMS)] (GP2)

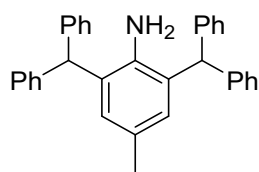


Az =



In a round bottom flask, [AuCl(DMS)] (1.00 eq.) was dissolved in reagent grade dichloromethane. Thereafter, the appropriate isonitrile (1.00 eq.) was added. After stirring the reaction mixture for one hour at room temperature, the amine (1.05 eq.) was added and the reaction was again stirred at room temperature upon completion. The crude reaction mixture was purified by flash column chromatography to obtain the corresponding azulene-tethered carbene gold(I) complex.

Synthesis of 2,6-dibenzhydryl-4-methylaniline

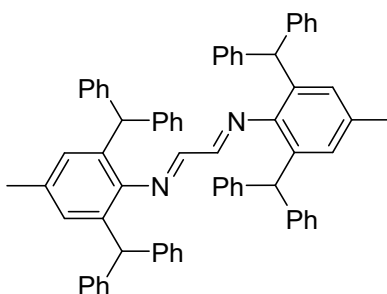


According to a literature procedure,^[1] *p*-toluidine (8.72 g, 81.4 mmol, 1.00 eq.), diphenylmethanol (30.0 g, 163 mmol, 2.00 eq.) were melted together at 80 °C. A solution of zinc chloride (5.55 g, 40.7 mmol, 50.0 mol%) and hydrochloric acid (36% in H₂O, 6.80 mL, 79.1 mmol, 97.0 mol%) was then added dropwise to the eutectic melt. Afterwards, the reaction mixture was stirred at 160 °C for 4 hours. After cooling to room temperature, the solidified reaction medium was taken up in dichloromethane (4 x 50 mL). The organic solution was washed subsequently with saturated solutions of ammonium chloride (200 mL) and brine (200 mL). The combined organic layers were dried over K₂CO₃. Evaporation of the solvent yielded the title compound as an off-white solid (35.3 g, 80.4 mmol, 98%).

The obtained ¹H NMR spectrum matched the reported literature data.^[1]

¹H NMR (CDCl₃, 300 MHz): δ [ppm] = 7.32 – 7.27 (m, 8H, 8xC_{Ar}H), 7.25 – 7.21 (m, 4H, 4xC_{Ar}H), 7.13 – 7.08 (m, 8H, 8xC_{Ar}H), 6.12 (s, 2H, 2xC_{Ar}H), 5.60 (s, 2H, -NH₂), 2.05 (s, 3H, -CH₃).

Synthesis of *N,N'*-bis(2,6-dibenzhydryl-4-methylphenyl)ethane-1,2-diimine

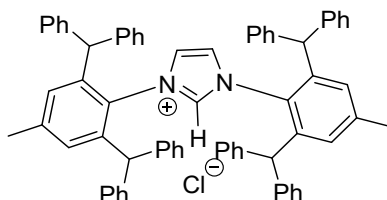


According to a literature procedure, 2,6-dibenzhydryl-4-methylaniline (17.0 g, 38.7 mmol, 2.00 eq.) was dissolved in acetonitrile (400 mL). Afterwards glyoxal (40% in H₂O, 2.81 g, 19.3 mmol, 1.00 eq.) and four drops of formic acid were added to the solution. The reaction mixture stirred for one week at 60 °C, at that the crude product participated which was filtered off and was washed subsequently with acetonitrile (3 x 50 mL) and concentrated *in vacuo*. The title compound was yielded as a yellow solid (11.0 g, 12.2 mmol, 63%).

The obtained ¹H NMR spectrum matched the reported literature data. ^[1]

¹H NMR (CDCl₃, 300 MHz, 295 K) δ [ppm] = 7.25 – 6.95 (m, 44H, 44xC_{Ar}H), 6.60 – 6.47 (m, 4H, 4xC_{Ar}H), 2.11 (s, 6H, 2x-CH₃).

Synthesis of 1,3-bis(2,6-bis(diphenylmethyl)-4-methylphenyl)-imidazolium chloride (IPr* HCl)

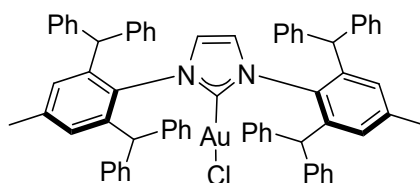


According to a literature procedure, *N,N'*-bis(2,6-dibenzhydryl-4-methylphenyl)ethane-1,2-diimine (7.00 g, 7.78 mmol, 1.00 eq.), ZnCl₂ (1.06 g, 7.77 mmol, 1.00 eq.) and paraformaldehyde (233 mg, 7.77 mmol, 1.00 eq.) were dissolved in chloroform (70.0 mL). The reaction mixture was stirred for 1 h at 60°C, afterwards the reaction mixture was concentrated *in vacuo*. The residue was taken up in ethyl acetate (70.0 mL), then TMSCl (844 mg, 7.77 mmol, 1.00 eq, dissolved in 5.00 mL EtOAc) was added to the solution. The reaction mixture was stirred overnight at 80 °C. Subsequently the solution was washed with water (2 x 50 mL) and brine (50 mL). The combined organic layers were dried over anhydrous MgSO₄ and then evaporated onto Celite ®. Purification of the crude product was obtained by flash column chromatography (Silica, dichloromethane → dichloromethane : MeOH = 95 :5). The title compound was obtained as an off-white solid (4.17 g, 4.40 mmol, 59%).

The obtained ¹H NMR spectrum matched the reported literature data.^[1]

¹H NMR (CDCl₃, 300 MHz, 295 K) δ [ppm] = 12.89 (s, 1H, C_{Carbene}H), 7.26 – 7.10 (m, 32H, 32xC_{Ar}H), 6.81 – 6.76 (m, 12H, 12xC_{Ar}H), 5.50 (s, 2H, 2xC_{Ar}H), 5.28 (s, 4H, 4xC_{Ar}H), 2.19 (s, 6H, 2x-CH₃).

Synthesis of (1,3-bis(2,6-dibenzhydryl-4-methylphenyl)-imidazol-2-ylidene)gold(I) chloride (IPr*AuCl)



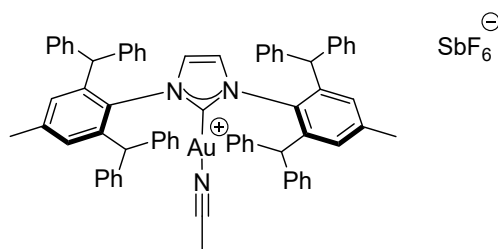
According to a literature procedure, [AuCl(DMS)] (200 mg, 679 μmol, 1.00 eq.), IPr* HCl (709 mg, 747 μmol, 1.10 eq.) and K₂CO₃ (141 mg, 1.02 mmol, 1.50 eq.) were suspended in acetone (15.0 mL) and stirred at room temperature overnight. The reaction mixture was concentrated *in*

vacuo and then evaporated onto Celite ®. Purification of the crude product was obtained by flash column chromatography (Silica, dichloromethane) to obtain the title compound as a colorless solid (651 mg, 569 µmol, 84%).

The obtained ¹H NMR spectrum matched the reported literature data.^[2]

¹H NMR (CD₂Cl₂, 300 MHz, 295 K) δ [ppm] = 7.27 – 7.01 (m, 32H), 6.98 – 6.82 (m, 12H), 5.85 (s, 2H), 5.27 (s, 4H), 2.17 (s, 6H)

Synthesis of [(IPr*)Au(NCMe)]SbF₆

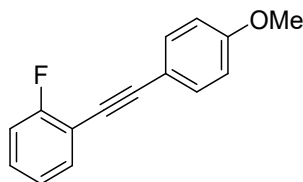


Based on a literature procedure, [AuCl(IPr*)] (170 mg, 148 µmol, 1.00 eq.) was dissolved in dry acetonitrile (3.00 mL), afterwards AgSbF₆ (53.5 mg, 156 µmol, 1.05 eq.) was added to the solution. The reaction mixture was stirred for 30 min at room temperature, then all the solvent was removed *in vacuo*. The residue was taken up in dichloromethane and filtered with dichloromethane (4 mL) through a plug of silica. Concentration *in vacuo* yielded the title compound as a colorless solid (199 mg, 143 µmol, 97%).

The obtained ¹H NMR spectrum matched the reported literature data.^[3]

¹H NMR (CD₂Cl₂, 300 MHz, 295 K) δ [ppm] = 7.30 – 7.15 (m, 24H, 24x C_{Ar}H), 6.95 – 6.86 (m, 20H, 20x C_{Ar}H), 6.11 (s, 2H, 2x C_{Ar}H), 5.08 (s, 4H, 4x C_{Ar}H), 2.44 (s, 3H, NCCH₃), 2.26 (s, 6H, 2x-CH₃).

Synthesis of 1-fluoro-2-((4-methoxyphenyl)ethynyl)benzene (1a)



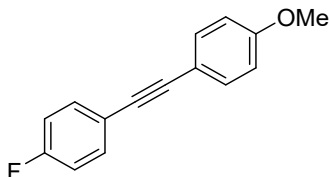
In a flame dried Schlenk-flask, 1-fluoro-2-iodobenzene (5.00 g, 22.5 mmol, 1.00 eq.), 1-ethynyl-4-methoxybenzene (3.57 g, 27.0 mmol, 1.20 eq.), bis(triphenylphosphine)palladium chloride (395 mg, 563 µmol, 2.50 mol%) and copper iodide (214 mg, 1.13 mmol, 5.00 mol%) were stirred at 60 °C in degassed triethylamine overnight. Afterwards, the reaction mixture was

purified by flash column chromatography (Silica, PE : EA = 30 : 1) to yield the title compound as a colourless solid (4.54 g, 20.1 mmol, 89%).

The obtained ^1H NMR spectrum matched the reported literature data.^[4]

^1H NMR (CDCl_3 , 300 MHz, 295 K) δ [ppm] = 7.54 – 7.48 (m, 3H, $3\times\text{C}_{\text{ArH}}$), 7.34 – 7.26 (m, 1H, C_{ArH}), 7.16 – 7.06 (m, 2H, $2\times\text{C}_{\text{ArH}}$), 6.93– 6.87 (m, 2H, $2\times\text{C}_{\text{ArH}}$), 3.85 (s, 3H, $-\text{OCH}_3$).

Synthesis of 1-fluoro-4-((4-methoxyphenyl)ethynyl)benzene (1b)

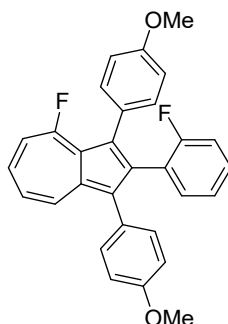


In a flame dried Schlenk-flask, 1-iodo-4-methoxybenzene (3.25 g, 13.9 mmol, 1.0 eq.), 1-ethynyl-4-fluorobenzene (2.00 g, 16.7 mmol, 1.2 eq.), bis(triphenylphosphine)palladium chloride (243 mg, 347 μmol , 2.5 mol%) and copper iodide (132 mg, 643 μmol , 5.0 mol%) were stirred at 80 °C in degassed triethylamine over night. Afterwards, the reaction mixture was purified by flash column chromatography (Silica, PE : EA = 100 : 1) to yield the title compound as a colourless solid (1.41 g, 72%).

The obtained ^1H NMR spectrum matched the reported literature data.^[4]

^1H NMR (CDCl_3 , 300 MHz, 295 K): δ [ppm] = 7.54 – 7.43 (m, 4H, $4\times\text{C}_{\text{ArH}}$), 7.10 – 6.99 (m, 2H, $2\times\text{C}_{\text{ArH}}$), 6.93 – 6.85 (m, 2H, $2\times\text{C}_{\text{ArH}}$), 3.84 (s, 3H, $-\text{OCH}_3$).

Synthesis of 4-fluoro-2-(2-(4-methoxyphenyl)ethynyl)-1,3-bis(4-methoxyphenyl)azulene (2a)

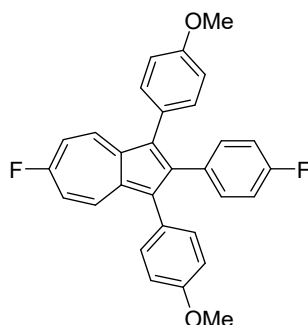


In a round bottom flask, 1-fluoro-2-((4-methoxyphenyl)ethynyl)benzene (**1a**) (3.50 g, 15.5 mmol, 2.0 eq.) and $[(\text{IPr}^*)\text{Au}(\text{NCMe})]\text{SbF}_6$ (536 mg, 387 μmol , 5.0 mol%) were stirred in toluene at 100 °C overnight. Afterwards, the reaction mixture was purified by flash column chromatography (Silica, petroleum ether : ethyl acetate = 50 : 1) to yield the title compound as a blue solid (2.87 g, 6.34 mmol, 82%).

The obtained ^1H NMR spectrum matched the reported literature data.^[4]

$^1\text{H}\{^{19}\text{F}\}$ NMR (300 MHz, CDCl_3 , 300 K) δ [ppm] = 8.26 (d, J = 9.9 Hz, 1H, $\text{C}_{\text{Ar}}\text{H}$), 7.42 (td, J = 10.28 Hz, 4.06 Hz, 1H, $\text{C}_{\text{Ar}}\text{H}$), 7.14 – 7.09 (m, 4H, $4\times\text{C}_{\text{Ar}}\text{H}$), 7.01 – 6.95 (m, 1H, $\text{C}_{\text{Ar}}\text{H}$), 6.92 (dd, J = 11.1 Hz, 3.4 Hz, 1H, $\text{C}_{\text{Ar}}\text{H}$), 6.88 – 6.82 (m, 3H, $3\times\text{C}_{\text{Ar}}\text{H}$), 6.82 – 6.78 (m, 3H, $3\times\text{C}_{\text{Ar}}\text{H}$), 6.71 (d, J = 8.67 Hz, 2H, $2\times\text{C}_{\text{Ar}}\text{H}$), 3.74 (s, 3H, $-\text{OCH}_3$), 3.73 (s, 3H, $-\text{OCH}_3$).

Synthesis of 6-fluoro-2-(4-fluorophenyl)-1,3-bis(4-methoxyphenyl)azulene (2b)

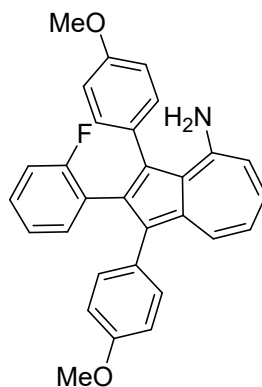


In a round bottom flask, 1-fluoro-4-((4-methoxyphenyl)ethynyl)benzene (**1b**) (3.70 g, 16.4 mmol, 2.00 eq.) and $[(\text{IPr}^*)\text{Au}(\text{NCMe})]\text{SbF}_6$ (567 mg, 408 μmol , 5.00 mol%) were stirred at 100 $^\circ\text{C}$ in toluene overnight. Afterwards, the reaction mixture was purified by flash column chromatography (Silica, PE : EA = 100 : 1) to yield the title compound as a blue solid (2.30 g, 62%).

The obtained ^1H NMR spectrum matched the reported literature data.^[4]

$^1\text{H}\{^{19}\text{F}\}$ NMR (300 MHz, CDCl_3 , 300 K) δ [ppm] = 8.30 – 8.15 (m, 2H, $2\times\text{C}_{\text{Ar}}\text{H}$), 7.24 – 7.11 (m, 4H, $4\times\text{C}_{\text{Ar}}\text{H}$), 7.10 – 6.78 (m, 10H, $10\times\text{C}_{\text{Ar}}\text{H}$), 3.86 (s, 6H, $2\times\text{OCH}_3$).

Synthesis of 2-(2-fluorophenyl)-1,3-bis(4-methoxyphenyl)azulen-4-amine (4a)

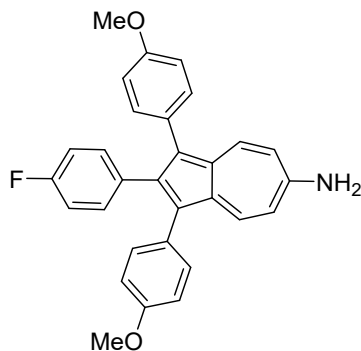


In a pressure vial, 4-fluoro-2-(2-fluorophenyl)-1,3-bis(4-methoxyphenyl)azulene (**2a**) (2.87 g, 6.34 mmol, 1.00 eq.) and ammonia (**3**) (21.58 g, 316 mmol, 50 eq., 25.0% in aq) were stirred

in acetonitrile at 100 °C for 12 h. Afterwards the solution was washed with brine (50 ml), the aqueous layer was extracted with dichloromethane (3x 30 mL). The combined organic layers were dried over anhydrous magnesium sulphate, filtered and concentrated *in vacuo*. Purification by flash column chromatography (Silica, PE : EA = 5 : 1) yielded the desired compound as a red (2.25 g, 5.01 mmol, 79%).

MP= 127 – 132 °C; **¹H{¹⁹F} NMR** (500 MHz, C₆D₆, 295 K) δ [ppm] = 8.14 (d, *J* = 10.0 Hz, 1H, C_{Ar}H), 7.18 (d, *J* = 8.8 Hz, 3H, 3x C_{Ar}H), 7.04 – 6.99 (m, 1H, C_{Ar}H), 6.95 (s, 1H, C_{Ar}H), 6.77 (ddd, *J* = 10.9, 9.1, 1.3 Hz, 1H, C_{Ar}H), 6.53 (d, *J* = 8.9 Hz, 2H, 2xC_{Ar}H), 6.50 – 6.47 (m, 2H, 2xC_{Ar}H), 6.47 – 6.37 (m, 3H, 3xC_{Ar}H), 6.26 (t, *J* = 9.5 Hz, 1H, C_{Ar}H), 5.57 (d, *J* = 11.1 Hz, 1H, C_{Ar}H), 4.35 (s, 2H, -NH₂), 3.02 (s, 3H, -OCH₃), 2.96 (s, 3H, -OCH₃); **¹³C{¹⁹F, ¹H} NMR** (126 MHz, C₆D₆, 295 K) δ [ppm] = 161.06 (s, 1C, C_{Ar}), 158.98 (s, 1C, C_{Ar}), 158.66 (s, 1C, C_{Ar}), 154.61 (s, 1C, C_{Ar}), 137.96 (s, 1C, C_{Ar}), 137.14 (d, 1C, C_{Ar}H), 136.97 (d, 1C, C_{Ar}H), 134.56 (s, 1C, C_{Ar}), 133.63 (d, 1C, C_{Ar}H), 133.27 (d, 1C, C_{Ar}H), 132.99 (d, 1C, C_{Ar}H), 132.83 (d, 1C, C_{Ar}H), 131.88 (s, 1C, C_{Ar}), 131.17 (s, 1C, C_{Ar}), 130.07 (d, 2C, 2xC_{Ar}H), 128.59 (d, 1C, C_{Ar}H), 128.44 (d, 1C, C_{Ar}H), 127.46 (s, 1C, C_{Ar}), 126.79 (s, 1C, C_{Ar}), 123.40 (s, 1C, C_{Ar}), 117.55 (s, 1C, C_{Ar}), 116.57 (d, 1C, C_{Ar}H), 116.08 (d, 1C, C_{Ar}H), 115.38 (d, 1C, C_{Ar}H), 113.88 (d, 2C, 2xC_{Ar}H), 113.37 (d, 1C, C_{Ar}H), 54.61 (q, 1C, .OCH₃), 54.58 (q, 1C, .OCH₃); **¹⁹F{¹H} NMR** (471 MHz, C₆D₆, 295 K) δ [ppm] = -111.74 (s, 1F, C_{Ar}F); **IR** (ATR) $\tilde{\nu}$ [cm⁻¹] = 3478 (m), 3452 (m), 3368 (m), 3360 (m), 3228 (m), 3001 (w), 2931 (w), 2836 (w), 1635 (m), 1606 (m), 1576 (m), 1546 (s), 1486 (m), 1430 (m), 1386 (w), 1302 (m), 1280 (m), 1232 (s), 1175 (s), 1155 (s), 1106 (s), 1038 (s), 949 (w), 889 (w), 840 (w), 811 (w), 774 (w), 726 (w), 624 (w); **HR-MS** (MALDI): C₃₀H₂₄FNO₂ [M]⁺ calcd.: 449.1791, found.: 449.1795, Δ*m/z* = 0.891 ppm; **UV/VIS** (CH₂Cl₂) λ_{max} (ε) [nm (l*mol⁻¹*cm⁻¹)] = 265 (39517), 313 (32571), 333 (28472), 398 (3093), 538 (1443).

Synthesis of 2-(4-fluorophenyl)-1,3-bis(4-methoxyphenyl)azulen-6-amine (4b)

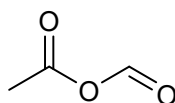


In a pressure vial, 6-fluoro-2-(4-fluorophenyl)-1,3-bis(4-methoxyphenyl)azulene (**2b**) (4.00 g, 8.84 mmol, 1.00 eq.) and ammonia (**3**) (30.1 g, 442 mmol, 50.0 eq., 25.0% in aq.) were stirred

in acetonitrile at 100 °C for 12 h. Afterwards the solution was washed with brine (50 ml), the aqueous layer was extracted with dichloromethane (3x 30 mL). The combined organic layers were dried over anhydrous magnesium sulphate, filtered and concentrated *in vacuo*. Purification by flash column chromatography (Silica, PE : EA = 3 : 1) yielded the desired compound as a red solid (3.07 g, 77%).

MP = 200 – 205 °C; **¹H{¹⁹F} NMR** (600 MHz, C₆D₆, 295 K) δ [ppm] = 8.17 (d, *J* = 11.0 Hz, 2H, 2x-C_{Ar}H), 7.33 (d, *J* = 8.8 Hz, 4H, 4x-C_{Ar}H), 7.21 (dd, *J* = 8.8, 5.5 Hz, 2H, 2x-C_{Ar}H), 6.68 (t, *J* = 8.8 Hz, 4H, 4x-C_{Ar}H), 5.77 (d, *J* = 11.0 Hz, 2H, 2x-C_{Ar}H), 3.33 (s, 6H, 2x-OCH₃), 3.21 (s, 2H, -NH₂); **¹³C{¹⁹F, ¹H} NMR** (151 MHz, C₆D₆, 295 K) δ [ppm] = 162.64 (s, 1C, -C_{Ar}), 161.02 (s, 1C, -C_{Ar}), 158.73 (d, 2C, 2x-C_{Ar}H), 157.01 (d, 2C, 2x-C_{Ar}H), 140.22 (s, 1C, -C_{Ar}), 136.98 (s, 2C, 2x-C_{Ar}), 134.41 (s, 1C, -C_{Ar}), 134.39 (s, 1C, -C_{Ar}), 133.42 (d, 1C, -C_{Ar}H), 133.37 (d, 1C, -C_{Ar}H), 132.97 (d, 2C, 2x-C_{Ar}H), 131.92 (s, 1C, -C_{Ar}), 130.38 (s, 1C, -C_{Ar}), 129.90 (s, 1C, -C_{Ar}), 128.59 (s, 1C, -C_{Ar}), 128.35 (s, 1C, -C_{Ar}), 115.05 (d, 2C, 2x-C_{Ar}H), 114.91 (d, 2C, 2x-C_{Ar}H), 114.13 (d, 2C, 2x-C_{Ar}H), 109.96 (d, 2C, 2x-C_{Ar}H), 54.76 (q, 2C, 2x-OCH₃); **¹⁹F{¹H} NMR** (283 MHz, C₆D₆, 295 K) δ [ppm] = -116.74 (s, 1F, C_{Ar}F); **IR** (ATR) $\tilde{\nu}$ [cm⁻¹] = 3361 (m), 3219 (w), 2960 (m), 2931 (m), 2874 (w), 2836 (w), 1581 (s), 1516 (s), 1463 (m), 1434 (m), 1407 (m), 1391 (m), 1287 (m), 1242 (s), 1221 (s), 1175 (s), 1156 (m), 1108 (8w), 1033 (m), 898 (w), 833 (m), 794 (m), 751 (w), 701 (w), 634 (w); **HR-MS** (EI+): C₃₀H₂₄FNO₂ [M]⁺ calcd.: 449.17911, found.: 449.17946, $\Delta m/z$ = 0.779 ppm; **UV/VIS** (CH₂Cl₂) $\lambda_{\max}$ (ϵ) [nm (l*mol⁻¹*cm⁻¹)] = 270 (1914), 343 (7614), 388 (806), 416 (31188), 479 (14373).

Synthesis of acetic formic anhydride (5)

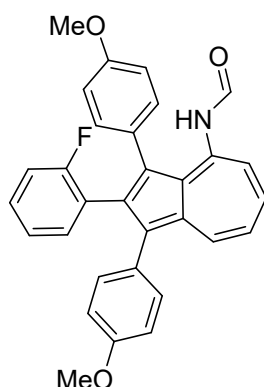


According to a literature procedure, sodium formate (22.0 g, 324 mmol, 1.20 eq.) was suspended in absolute diethylether (20.0 mL). Then acetic chloride (21.2 g, 270 mmol, 1.00 eq.) was added to dropwise. The reaction mixture was stirred over night at room temperature, afterwards the solid was filtered off. The crude product was concentrated *in vacuo* and was used without further purification. The reaction yielded the title compound as a colorless fluid (18.5 g, 78%).

The obtained ¹H NMR spectrum matched the reported literature data.^[5]

¹H NMR (CDCl₃, 300 MHz): δ [ppm] = 9.03 (s, 1H), 2.21 (s, 3H).

Synthesis of N-(2-(2-fluorophenyl)-1,3-bis(4-methoxyphenyl)azulen-4-yl)formamide (6a)

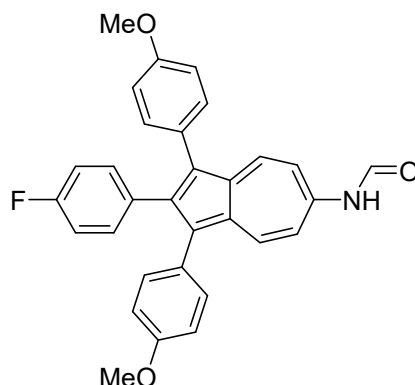


In a round bottom flask, 2-(2-fluorophenyl)-1,3-bis(4-methoxyphenyl)azulen-4-amine (**4a**) (2.10 g, 4.67 mmol, 1.00 eq.) was dissolved in anhydrous dichloromethane, afterwards acetic formic anhydride (**5**) (411 mg, 4.67 mmol, 1.00 eq.) was added dropwise to the solution. The reaction was stirred at room temperature for 1 h. Afterwards, the reaction mixture was quenched by the addition of aqueous sodium carbonate and the aqueous layer was extracted with dichloromethane (3x50 mL). The combined organic layers were dried over anhydrous magnesium sulphate, filtered and concentrated *in vacuo*. Purification by flash column chromatography (Silica, dichloromethane : petroleum ether = 1:1) yielded the desired product as a green solid (1.67 g, 3.50 mmol, 75%).

MP = 173 – 178 °C; **¹H{¹⁹F} NMR** (700 MHz, C₂D₂Cl₄, 400 K) δ [ppm] = 8.42 (s, 1H, -NHCHO), 8.34 (d, *J* = 9.5 Hz, 1H, C_{Ar}H), 8.08 – 8.05 (m, 1H, -NHCHO), 7.70 (s, 1H, C_{Ar}H), 7.58 (t, *J* = 10.3 Hz, 1H, C_{Ar}H), 7.29 (d, *J* = 8.4 Hz, 2H, 2xC_{Ar}H), 7.25 (d, *J* = 8.6 Hz, 2H, C_{Ar}H), 7.15 (m, 1H, C_{Ar}H), 7.07 (t, *J* = 9.6 Hz, 1H, C_{Ar}H), 7.01 – 6.97 (m, 1H, C_{Ar}H), 6.95 – 6.90 (m, 5H, 5xC_{Ar}H), 6.88 (t, *J* = 9.0 Hz, 1H, C_{Ar}H), 3.87 (s, 6H, 2x-CH₃); **¹³C{¹H} NMR** (176 MHz, C₂D₂Cl₄, 400 K) δ [ppm] = 160.70 (s, 1C, C_{Ar}), 159.74 (d, 1C, -NHCHO), 159.29 (s, 1C, C_{Ar}), 158.56 (s, 1C, C_{Ar}), 143.24 (s, 1C, C_{Ar}), 142.75 (s, 1C, C_{Ar}), 138.09 (s, 1C, C_{Ar}), 136.82 (d, 1C, C_{Ar}H), 136.45 (d, 1C, C_{Ar}H), 132.40 (d, 1C, C_{Ar}H, d, *J* = 3.7 Hz), 132.36 (d, 1C, C_{Ar}H), 131.99 (d, 1C, C_{Ar}H), 131.74 (s, 1C, C_{Ar}), 129.14 (s, 1C, C_{Ar}), 128.49 (d, 1C, C_{Ar}H, d, *J* = 7.8 Hz), 128.27 (s, 1C, C_{Ar}), 127.21 (s, 1C, C_{Ar}), 124.80 (s, 1C, C_{Ar}, d, *J* = 16.5 Hz), 123.46 (s, 1C, C_{Ar}), 122.79 (d, 1C, C_{Ar}H, d, *J* = 3.4 Hz), 121.29 (d, 1C, C_{Ar}H), 116.69 (d, 1C, C_{Ar}H), 114.76 (d, 1C, C_{Ar}H), 114.64 (d, 1C, C_{Ar}H, *J* = 22.3 Hz), 113.79 (d, 1C, C_{Ar}H), 113.67 (d, 1C, C_{Ar}H), 55.27 (q, 1C, -OCH₃), 55.15 (q, 1C, -OCH₃); **¹⁹F{¹H} NMR** (471 MHz, C₆D₆, 295 K) δ [ppm] = -111.83 (s, 1F, C_{Ar}F); **IR** (ATR) $\tilde{\nu}$ [cm⁻¹] = 3354 (m), 2933 (w), 2836 (w), 1691 (s), 1607 (m), 1577 (m), 1547 (s), 1454 (m), 1263 (s), 1242 (s), 1177 (s), 1107 (s), 1030 (s), 949 (w), 933 (w), 833 (w), 752 (w), 736 (w), 667 (w); **HR-MS** (EI⁺): C₃₁H₂₄FNO₃ [M]⁺ calcd.:

477.17402, found.: 477.17237, $\Delta m/z = 3.457$ ppm ; UV/VIS (CH₂Cl₂) $\lambda_{\max}$ (ϵ) [nm (l*mol⁻¹*cm⁻¹)] = 270 (101373), 319 (89643), 369 (91319), 590 (1198), 638 (184).

Synthesis of N-(2-(4-fluorophenyl)-1,3-bis(4-methoxyphenyl)azulen-6-yl)formamide (6b)

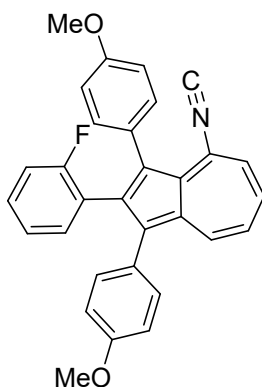


In a round bottom flask, 2-(4-fluorophenyl)-1,3-bis(4-methoxyphenyl)azulen-6-amine (**4b**) (6.00 g, 13.4 mmol, 1.00 eq.) was dissolved in anhydrous dichloromethane, afterwards acetic formic anhydride (**5**) (1.18 g, 13.4 mmol, 1.00 eq.) was added dropwise to the solution. The reaction was stirred at room temperature for 1 h. Afterwards, the reaction mixture was quenched by the addition of aqueous sodium carbonate and the aqueous layer was extracted with dichloromethane (3x50 mL). The combined organic layers were dried over anhydrous magnesium sulphate, filtered and concentrated *in vacuo*. Purification by flash column chromatography (Silica, dichloromethane : petroleum ether = 1:1) yielded the desired product as a green solid (5.70 g, 11.9 mmol, 89%).

MP = 231 – 236 °C; **¹H{¹⁹F} NMR** (700 MHz, C₂D₂Cl₄, 295 K) δ [ppm] = 8.88 (d, $J = 10.8$ Hz, 1H, -NHCHO, major rotamer), 8.43 (s, 1H, -NHCHO, minor rotamer), 8.19 (t, $J = 10.6$ Hz, 1H, 2xC_{Ar}H), 7.98 (d, $J = 10.8$ Hz, 1H, -NHCHO, major rotamer), 7.40 (s, 1H, -NHCHO, minor rotamer), 7.35 (d, $J = 10.8$ Hz, 1H, C_{Ar}H), 7.17 (d, $J = 8.7$ Hz, 4H, 4xC_{Ar}H), 7.00 – 6.96 (m, 2H, 2xC_{Ar}H), 6.92 (d, $J = 8.6$ Hz, 4H, 4xC_{Ar}H), 6.86 (t, $J = 8.8$ Hz, 2H, 2xC_{Ar}H), 6.75 (d, $J = 11.0$ Hz, 1H, C_{Ar}H), 3.85 (s, 6H, 2x-OCH₃); **¹³C{¹H} NMR** (151 MHz, CD₂Cl₂, 295 K) δ [ppm] = (176 MHz, C₂D₂Cl₄, 400 K) δ [ppm] = 162.16 (d, 1C, -NHCHO, major rotamer), 162.09 (s, 1C, C_{Ar}), 160.67 (s, 1C, C_{Ar}, $J = 7.8$ Hz), 159.27 (d, 1C, -NHCHO, minor rotamer), 158.03 (s, 1C, C_{Ar}), 157.91 (s, 1C, C_{Ar}), 145.30 (s, 1C, C_{Ar}), 145.17 (s, 1C, C_{Ar}), 144.85 (s, 1C, C_{Ar}), 144.16 (s, 1C, C_{Ar}), 135.35 (d, 1C, C_{Ar}H), 135.16 (d, 1C, C_{Ar}H), 134.55 (s, 1C, C_{Ar}), 134.26 (s, 1C, C_{Ar}), 132.72 (d, 1C, C_{Ar}H, $J = 7.4$ Hz), 132.29 (d, 1C, C_{Ar}H), 132.26 (d, 2C, 2xC_{Ar}H), 132.14 (d, 1C, C_{Ar}H), 130.60 (d, 1C, C_{Ar}H), 129.76 (d, 1C, C_{Ar}H), 127.77 (s, 1C, C_{Ar}), 127.55 (d, 1C, C_{Ar}H), 120.18 (s, 1C, C_{Ar}), 115.28 (d, 1C, C_{Ar}H), 114.69 (d, 1C, C_{Ar}H, $J = 9.8$ Hz),

114.57 (d, 1C, $\underline{C}_{Ar}H$, d, $J = 9.8$ Hz), 113.65 (d, 1C, $\underline{C}_{Ar}H$), 113.58 (d, 1C, $\underline{C}_{Ar}H$), 113.16 (d, 1C, $\underline{C}_{Ar}H$), 55.24 (q, 2C, 2x-OCH₃); $^{19}F\{^1H\}$ NMR (283 MHz, CD₂Cl₂, 295 K) δ [ppm] = -116.37 (s, 1F, $\underline{C}_{Ar}F$); IR (ATR) $\tilde{\nu}$ [cm⁻¹] = 3006 (w), 2959(w), 2927 (w), 2853 (w), 1741 (w), 1684 (s), 1608 (w), 1572 (m), 1548 (m), 1519 (s), 1441 (m), 1407 (w), 1388 (w), 1288 (s), 1245 (s), 1221 (s), 1175 (m), 1156 (m), 1108 (w), 1093 (w), 1033 (m), 909 (w), 826 (m), 796 (m), 751 (w), 637 (w); HR-MS (EI⁺): C₃₁H₂₄FNO₃ [M]⁺ calcd.: 477.17402, found.: 477.17208, $\Delta m/z = 4.07$ ppm.

Synthesis of 2-(2-fluorophenyl)-4-isocyano-1,3-bis(4-methoxyphenyl)azulene (10a)

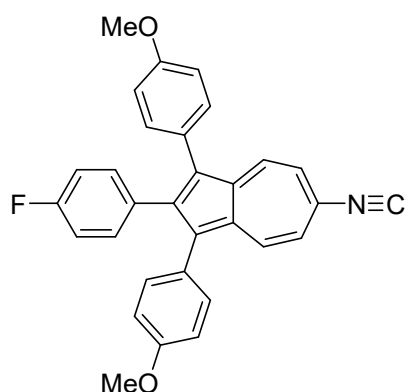


In a round bottom flask, *N*-(2-(4-fluorophenyl)-1,3-bis(4-methoxyphenyl)azulen-6-yl)formamide (**6a**) (1.16 g, 2.43 mmol, 1.00 eq.) was dissolved in reagent grade dichloromethane. Afterwards, triphenylphosphine (**7**) (1.91 g, 7.29 mmol, 3.00 eq.) and iodine (**8**) (1.85 g, 7.29 mmol, 3.00 eq.) were added to the solution. To the solution triethylamine (**9**) (1.47 g, 14.6 mmol, 6.00 eq.) was added dropwise at room temperature. After stirring for 3 h at room temperature, the reaction mixture was quenched by the addition of an aqueous sodium thiosulphate solution. The aqueous layer was extracted with dichloromethane (3x50 mL). The combined organic layers were then dried over anhydrous magnesium sulphate, filtered and concentrated *in vacuo*. Purification by flash column chromatography (Silica, PE : NEt₃ = 95 : 5) yielded the desired product as a green solid (825 mg, 1.80 mmol, 73%).

MP= 116 – 121 °C; $^1H\{^{19}F\}$ NMR (500 MHz, C₆D₆, 295 K) δ [ppm] = 8.23 (dd, $J = 9.5$, 1.1 Hz, 1H, $\underline{C}_{Ar}H$), 7.39 – 7.32 (m, 1H, $\underline{C}_{Ar}H$), 7.25 (d, $J = 8.6$ Hz, 3H, 3x $\underline{C}_{Ar}H$), 7.05 (dd, $J = 7.5$, 1.9 Hz, 1H, $\underline{C}_{Ar}H$), 6.89 – 6.83 (m, 1H, $\underline{C}_{Ar}H$), 6.82 – 6.74 (m, 4H, 4x $\underline{C}_{Ar}H$), 6.73 – 6.69 (m, 1H, $\underline{C}_{Ar}H$), 6.68 (s, 1H, $\underline{C}_{Ar}H$), 6.66 (s, 1H, $\underline{C}_{Ar}H$), 6.65 – 6.61 (m, 1H, $\underline{C}_{Ar}H$), 6.53 (t, $J = 9.6$ Hz, 1H, $\underline{C}_{Ar}H$), 3.25 (s, 3H, -OCH₃), 3.23 (s, 3H, -OCH₃); $^{13}C\{^{19}F, ^1H\}$ NMR (101 MHz, C₆D₆, 295 K) δ [ppm] = 174.88 (s, 1C, $\underline{C}_{Ar}$), 161.74 (s, 1C, $\underline{C}_{Ar}$), 159.67 (s, 1C, $\underline{C}_{Ar}$), 159.38 (s, 1C, $\underline{C}_{Ar}$), 159.29 (s, 1C, $\underline{C}_{Ar}$), 147.53 (s, 1C, $\underline{C}_{Ar}$), 139.31 (s, 1C, $\underline{C}_{Ar}$), 136.88 (d, 1C, $\underline{C}_{Ar}H$), 135.73

(d, 1C, $\underline{C_{Ar}H}$), 133.11 (d, 1C, $\underline{C_{Ar}H}$), 132.82 (d, 1C, $\underline{C_{Ar}H}$), 132.78 (d, 1C, $\underline{C_{Ar}H}$), 132.62 (s, 1C, $\underline{C_{Ar}}$), 132.51 (d, 1C, $\underline{C_{Ar}H}$), 131.41 (s, 1C, $\underline{C_{Ar}}$), 130.92 (s, 1C, $\underline{C_{Ar}}$), 129.63 (d, 1C, $\underline{C_{Ar}H}$), 129.55 (d, 1C, $\underline{C_{Ar}H}$), 128.59 (d, 1C, $\underline{C_{Ar}H}$), 127.27 (s, 1C, $\underline{C_{Ar}}$), 125.26 (s, 1C, $\underline{C_{Ar}}$), 125.09 (s, 1C, $\underline{C_{Ar}}$), 124.31 (d, 1C, $\underline{C_{Ar}H}$), 123.92 (d, 1C, $\underline{C_{Ar}H}$), 123.66 (d, 1C, $\underline{C_{Ar}H}$), 115.72 (d, 1C, $\underline{C_{Ar}H}$), 115.50 (d, 1C, $\underline{C_{Ar}H}$), 114.21 (d, 1C, $\underline{C_{Ar}H}$), 113.23 (d, 1C, $\underline{C_{Ar}H}$), 54.72 (q, 1C, $-OCH_3$), 54.57; $^{19}F\{^1H\}$ NMR (471 MHz, C_6D_6 , 295 K) δ [ppm] = -111.65 (s, 1F, $C_{Ar}F$); IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2966 (w), 2925 (w), 2835 (w), 2535 (w), 2109 (s), 1949 (w), 1763 (w), 1688 (m), 1639 (m), 1588 (m), 1578 (m), 1544 (s), 1447 (m), 1407 (m), 1365 (w), 1265 (s), 1242 (s), 1226 (s), 1176 (s), 1127 (s), 1105 (s), 1039 (s), 980 (m), 938 (w), 880 (w), 828 (w), 802 (w), 761 (w), 739 (w), 721 (w), 693 (w), 619 (w); HR-MS (EI⁺): $C_{31}H_{22}FNO_2$ [M]⁺ calcd.: 459.16346, found.: 459.16318, $\Delta m/z$ = 0.610 ppm; UV/VIS (CH_2Cl_2) λ_{max} (ϵ) [nm ($l \cdot mol^{-1} \cdot cm^{-1}$)] = 259 (49396), 294 (64330), 324 (90751), 412 (10339), 647 (574).

Synthesis of 2-(4-fluorophenyl)-6-isocyano-1,3-bis(4-methoxyphenyl)azulene (10b)

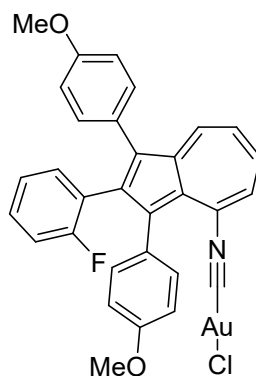


In a round bottom flask, *N*-(2-(4-fluorophenyl)-1,3-bis(4-methoxyphenyl)azulen-6-yl)formamide (**6b**) (5.70 g, 11.9 mmol, 1.00 eq.) was dissolved in reagent grade dichloromethane. Afterwards, triphenylphosphine (**7**) (9.39 g, 35.8 mmol, 3.00 eq.) and iodine (**8**) (9.09 g, 35.8 mmol, 3.00 eq.) were added to the solution. To the solution triethylamine (**9**) (7.25 g, 71.6 mmol, 6.00 eq.) was added dropwise at room temperature. After stirring for 3 h at room temperature, the reaction mixture was quenched by the addition of an aqueous sodium thiosulphate solution. The aqueous layer was extracted with dichloromethane (3x50 mL). The combined organic layers were then dried over anhydrous magnesium sulphate, filtered and concentrated *in vacuo*. Purification by flash column chromatography (Silica, PE : NEt_3 = 95 : 5) yielded the desired product as a green solid (5.20 g, 11.3 mmol, 95%).

MP = 127 – 132 °C; $^1H\{^{19}F\}$ NMR (400 MHz, CD_2Cl_2 , 295 K) δ [ppm] = 8.15 (d, J = 10.7 Hz, 2H, $2 \times C_{Ar}H$), 7.15 (d, J = 8.9 Hz, 4H, $4 \times C_{Ar}H$), 7.07 (d, J = 10.8 Hz, 2H, $2 \times C_{Ar}H$), 7.03 (dd, J

= 9.0, 5.5 Hz, 2H, 2xC_{ArH}), 6.93 (d, *J* = 8.8 Hz, 4H, 4xC_{ArH}), 6.86 (t, *J* = 8.9 Hz, 2H, 2xC_{ArH}), 5.33 (s, 3H, -OCH₃), 3.84 (s, 3H, -OCH₃); ¹³C{¹⁹F, ¹H} NMR (101 MHz, CD₂Cl₂, 295 K) δ [ppm] = 165.35 (s, 1C, C_{Ar}), 163.68 (s, 1C, C_{Ar}), 161.22 (s, 1C, C_{Ar}), 159.28 (s, 2C, 2xC_{Ar}), 149.40 (s, 1C, C_{Ar}), 137.28 (s, 1C, C_{Ar}), 134.36 (d, 2C, 2xC_{ArH}), 133.37 (d, 2C, 2xC_{ArH}), 133.29 (d, 2C, 2xC_{ArH}), 132.79 (d, 2C, 2xC_{ArH}), 132.56 (s, 2C, 2xC_{Ar}), 132.52 (s, 1C, C_{Ar}), 131.76 (s, 1C, C_{Ar}), 127.65 (s, 2C, 2xC_{Ar}), 121.40 (d, 2C, 2xC_{ArH}), 115.29 (d, 2C, 2xC_{ArH}), 115.08 (d, 2C, 2xC_{ArH}), 114.23 (d, 2C, 2xC_{ArH}), 55.65 (q, 2C, 2x-OCH₃); ¹⁹F{¹H} NMR (283 MHz, CD₂Cl₂, 298 K) δ [ppm] = -115.27 (s, 1F, -C_{ArF}); IR (ATR) $\tilde{\nu}$ [cm⁻¹] = 2957 (w), 2929 (w), 2852 (w), 2836 (w), 2108 (s), 1727 (w), 1605 (m), 1573 (m), 1537 (w), 1517 (s), 1441 (s), 1406 (m), 1385 (w), 1287 (m), 1244 (s), 1174 (s), 1157 (m), 1132 (w), 1107 (w), 1031 (s), 951 (w), 834 (s), 793 (s), 753 (w), 657 (w); HR-MS (EI⁺): C₃₁H₂₂FNO₂ [M]⁺ calcd.: 459.16346, found.: 459.16382, Δ*m/z* = 0.784 ppm; UV/VIS (CH₂Cl₂) λ_{max} (ε) [nm (l*mol⁻¹*cm⁻¹)] = 259 (49396), 294 (64330), 324 (90751), 412 (10339), 647 (574).

Synthesis of 2-(2-fluorophenyl)-4-isocyano-1,3-bis(4-methoxyphenyl)azulene gold(I)chloride (12a)

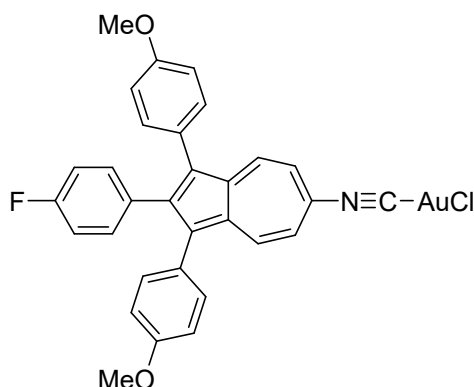


In a round bottom flask, [AuCl(DMS)] (**11**) (224 mg, 762 μmol, 1.00 eq.) and 2-(2-fluorophenyl)-4-isocyano-1,3-bis(4-methoxyphenyl)azulene (**10a**) (350 mg, 762 μmol, 1.00 eq.) were dissolved in reagent grade dichloromethane. The reaction mixture was stirred at room temperature for 1 h. Purification by flash column chromatography (Silica, dichloromethane : petroleum ether = 1 : 1) yielded the desired product as a green solid (427 mg, 617 μmol, 81%).

MP = 147 – 152 °C; ¹H{¹⁹F} NMR (700 MHz, C₆D₆, 295 K) δ [ppm] = 8.13 (d, *J* = 9.5 Hz, 1H), 7.20 (d, *J* = 8.3 Hz, 2H), 7.09 – 7.03 (m, 1H), 7.00 (t, *J* = 7.4 Hz, 1H), 6.96 – 6.92 (m,

1H), 6.85 – 6.81 (m, 1H), 6.75 (d, $J = 7.8$ Hz, 3H), 6.69 (t, $J = 10.1$ Hz, 2H), 6.62 (q, $J = 8.4$ Hz, 2H), 6.55 (t, $J = 9.8$ Hz, 1H), 6.23 (d, $J = 10.2$ Hz, 1H), 3.69 (s, 6H), 3.25 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, C_6D_6 , 295 K) δ [ppm] = 160.97 (s, 1C), 160.72 (s, 1C), 159.58 (s, 1C), 148.41 (s, 1C), 145.83 (s, 1C), 139.20 (s, 1C), 137.01 (d, 1C), 135.20 (d, 1C), 133.04 (s, 1C), 132.67 (d, 1C), 132.41 (d, 1C), 131.24 (s, 1C), 130.07 (d, 1C), 130.03 (d, 1C), 128.59 (d, 1C), 128.35 (d, 1C), 127.31 (s, 1C), 127.26 (s, 1C), 127.07 (s, 1C), 125.33 (d, 1C), 124.43 (s, 1C), 124.34 (s, 1C), 123.81 (d, 1C), 123.79 (d, 1C), 123.02 (d, 1C), 115.80 (d, 1C), 115.68 (d, 1C), 114.32 (d, 1C), 114.13 (d, 1C), 55.27 (q, 1C), 54.74 (q, 1C); $^{19}\text{F}\{^1\text{H}\}$ NMR (283 MHz, C_6D_6 , 295 K) δ [ppm] = -111.67; IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2956, 2932, 2904, 2835, 2534, 2204, 1608, 1561, 1522, 1481, 1449, 1405, 1357, 1288, 1245, 1208, 1175, 1107, 1093, 1030, 941, 864, 830, 792, 760, 728, 701, 628; HR-MS (MALDI): $\text{C}_{31}\text{H}_{22}\text{Au}^{35}\text{ClFNO}_2$ $[\text{M}]^+$ calcd.: 691.0989, found.: 691.1006, $\Delta m/z = 2.460$ ppm; UV/VIS (CH_2Cl_2) λ_{max} (ϵ) [nm ($\text{l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$)] = 269 (69771), 329 (61698), 664 (6285), 711 (1649), 800 (254).

Synthesis of 2-(4-fluorophenyl)-6-isocyano-1,3-bis(4-methoxyphenyl)azulene gold(I)chloride (**12b**)

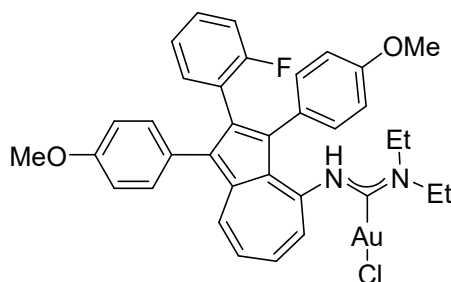


In a round bottom flask, $[\text{AuCl}(\text{DMS})]$ (**11**) (641 mg, 2.18 mmol, 1.00 eq.) and 2-(4-fluorophenyl)-6-isocyano-1,3-bis(4-methoxyphenyl)azulene (**10b**) (1.00 g, 2.18 mmol, 1.00 eq.) were dissolved in reagent grade dichloromethane. The reaction mixture was stirred at room temperature for 1 h. Purification by flash column chromatography (Silica, dichloromethane : petroleum ether = 1 : 1) yielded the desired product as a green solid (1.12 g, 1.62 mmol, 74%).

MP = 151 – 156 °C; $^1\text{H}\{^{19}\text{F}\}$ NMR (400 MHz, CD_2Cl_2 , 295 K) δ [ppm] = 8.19 (d, $J = 10.7$ Hz, 2H, $2\times\text{C}_{\text{ArH}}$), 7.18 – 7.13 (m, 5H, $5\times\text{C}_{\text{ArH}}$), 7.12 (s, 1H, C_{ArH}), 7.03 (dd, $J = 9.0, 5.5$ Hz, 2H, $2\times\text{C}_{\text{ArH}}$), 6.94 (d, $J = 8.9$ Hz, 4H, $4\times\text{C}_{\text{ArH}}$), 6.87 (t, $J = 8.9$ Hz, 2H, $2\times\text{C}_{\text{ArH}}$), 3.84 (s, 6H, $2\times\text{-OCH}_3$); $^{13}\text{C}\{^{19}\text{F}, ^1\text{H}\}$ NMR (101 MHz, CD_2Cl_2 , 295 K) δ [ppm] = 163.89 (s, 1C, CN), 161.43

(s, 2C, 2xC_{Ar}), 159.51 (s, 2C, 2xC_{Ar}), 151.32 (s, 2C, 2xC_{Ar}), 137.90 (s, 2C, 2xC_{Ar}), 134.01 (d, 2C, 2xC_{Ar}H), 133.40 (d, 2C, 2xC_{Ar}H), 133.32 (d, 2C, 2xC_{Ar}H), 132.91 (s, 2C, 2xC_{Ar}), 132.78 (d, 2C, 2xC_{Ar}H), 127.14 (s, 2C, 2xC_{Ar}), 120.96 (d, 2C, 2xC_{Ar}H), 115.45 (d, 2C, 2xC_{Ar}H), 115.23 (d, 2C, 2xC_{Ar}H), 114.36 (d, 2C, 2xC_{Ar}H), 55.69 (q, 2C, 2x-OCH₃); ¹⁹F{¹H} NMR (283 MHz, CD₂Cl₂, 298 K) δ [ppm] = -114.59 (s, 1F, C_{Ar}F); IR (ATR) $\tilde{\nu}$ [cm⁻¹] = 3028 (w), 3005 (w), 2962 (w), 2931 (w), 2904 (w), 2834 (w), 2207 (m), 2045 (w), 1732 (m), 1605 (m), 1569 (w), 1514 (s), 1442 (m), 1403 (m), 1289 (m), 1247 (s), 1227 (s), 1173 (s), 1156 (m), 1108 (m), 1029 (s), 948 (w), 853 (s), 838 (s), 827 (s), 794 (s), 739 (s), 697 (w), 631 (w), 609 (w); HR-MS (MALDI): C₃₁H₂₂AuClFNO₂ [M]⁺ calcd.: 691.0989, found.: 691.0991, Δm/z = 0.289 ppm; UV/VIS (CH₂Cl₂) λ_{max} (ε) [nm (l*mol⁻¹*cm⁻¹)] = 263 (27258), 334 (59758), 432 (8177), 683 (325), 741 (283).

Synthesis of ((diethylamino)((2-(2-fluorophenyl)-1,3-bis(4-methoxyphenyl)azulen-4-yl)amino)methylene)gold(I) chloride (14aa)



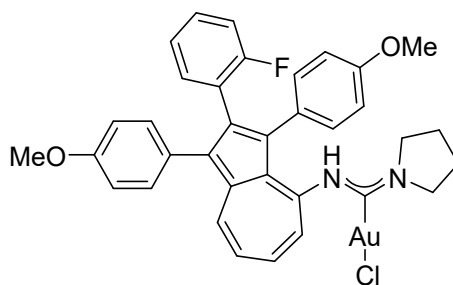
According to **GP1** 2-(2-fluorophenyl)-4-isocyano-1,3-bis(4-methoxyphenyl)azulene gold(I)chloride (**12a**) (50.0 mg, 72.3 μmol, 1.0 eq.) and diethylamine (**13a**) (5.55 mg, 75.9 μmol, 1.05 eq.) was stirred in dichloromethane at room temperature 12 hours. Purification by flash column chromatography (Silica, dichloromethane) yielded the title compound as a blue solid (37.0 mg, 72.3 μmol, 67%).

According to **GP2** [AuCl(DMS)] (**11**) (52.6 mg, 179 μmol, 1.00 eq.) and 2-(2-fluorophenyl)-4-isocyano-1,3-bis(4-methoxyphenyl)azulene (**10a**) (82.0 mg, 178 μmol, 1.00 eq.) were stirred in dichloromethane for 1 hour at room temperature. Afterwards, diethylamine (**13a**) (13.7 mg, 187 μmol, 1.05 eq.) was added, the mixture stirred at room temperature for additional 12 hours. Purification by flash column chromatography (Silica, dichloromethane) yielded the title compound as a blue solid (91.0 mg, 119 μmol, 67%).

MP = 189 – 194 °C; ¹H{¹⁹F} NMR (500 MHz, C₆D₆, 295 K) δ [ppm] = 8.11 (dd, *J* = 9.6, 1.1 Hz, 1H, C_{Ar}H), 7.69 (d, *J* = 10.6 Hz, 1H, C_{Ar}H), 7.15 (d, *J* = 8.4 Hz, 2H, 2xC_{Ar}H), 7.10 – 7.03 (m, 1H, C_{Ar}H), 6.99 (s, 1H, NH), 6.82 (ddd, *J* = 9.4, 7.9, 2.0 Hz, 2H, 2xC_{Ar}H), 6.73 (dd, *J* =

8.4, 2.3 Hz, 1H, C_{Ar}H), 6.60 (d, $J = 8.9$ Hz, 2H, 2xC_{Ar}H), 6.56 (ddd, $J = 8.7, 7.0, 1.7$ Hz, 1H, C_{Ar}H), 6.53 – 6.42 (m, 3H, 3xC_{Ar}H), 6.28 (dd, $J = 8.5, 2.9$ Hz, 1H, C_{Ar}H), 6.23 (dd, $J = 8.5, 2.9$ Hz, 1H, C_{Ar}H), 3.43 (dq, $J = 14.2, 7.2$ Hz, 1H, -CH₂-), 3.13 (dt, $J = 13.5, 7.1$ Hz, 1H, -CH₂-), 3.09 (s, 3H, -OCH₃), 2.98 (s, 3H, -OCH₃), 1.47 (dq, $J = 14.8, 7.3$ Hz, 1H, -CH₂-), 1.35 (dq, $J = 14.6, 7.2$ Hz, 1H, -CH₂-), 0.62 (t, $J = 7.2$ Hz, 3H, -CH₃), 0.03 (t, $J = 7.3$ Hz, 3H, -CH₃); ¹³C{¹⁹F, ¹H} NMR (126 MHz, C₆D₆, 295 K) δ [ppm] = 191.52 (s, 1C, C_{Carbene}), 161.68 (s, 1C, C_{Ar}), 159.72 (s, 1C, C_{Ar}), 159.22 (s, 1C, C_{Ar}), 158.80 (s, 1C, C_{Ar}), 146.41 (s, 1C, C_{Ar}), 143.66 (s, 1C, C_{Ar}), 138.88 (s, 1C, C_{Ar}), 137.43 (d, 1C, C_{Ar}H), 136.60 (d, 1C, C_{Ar}H), 134.23 (d, 1C, C_{Ar}H), 133.10 (d, 1C, C_{Ar}H), 132.99 (d, 1C, C_{Ar}H), 132.59 (d, 1C, C_{Ar}H), 132.41 (s, 1C, C_{Ar}), 129.55 (s, 1C, C_{Ar}), 129.30 (d, 1C, C_{Ar}H), 128.59 (d, 1C, C_{Ar}H), 127.47 (s, 1C, C_{Ar}), 126.64 (s, 1C, C_{Ar}), 125.75 (s, 1C, C_{Ar}), 123.78 (d, 1C, C_{Ar}H), 123.53 (d, 1C, C_{Ar}H), 123.21 (d, 1C, C_{Ar}H), 115.68 (d, 1C, C_{Ar}H), 115.51 (d, 1C, C_{Ar}H), 114.20 (d, 1C, C_{Ar}H), 113.59 (d, 1C, C_{Ar}H), 113.47 (d, 1C, C_{Ar}H), 54.83 (q, 1C, -OCH₃), 54.74 (q, 1C, -OCH₃), 54.02 (t, 1C, -CH₂-), 40.15 (t, 1C, -CH₂-), 14.39 (q, 1C, -CH₃), 11.09 (q, 1C, -CH₃); ¹⁹F{¹H} NMR (471 MHz, C₆D₆, 295 K) δ [ppm] = -112.06 (s, 1F, C_{Ar}F); IR (ATR) $\tilde{\nu}$ [cm⁻¹] = 3317, 2973, 2932, 2834, 1731, 1607, 1568, 1539, 1516, 1479, 1450, 1383, 1345, 1324, 1285, 1243, 1210, 1175, 1106, 1092, 1030, 934, 832, 812, 792, 764, 754, 730, 638; HR-MS (MALDI): C₃₅H₃₃AuClFN₂O₂ [M]⁺ calcd.: 764.1880, found.: 764.1875, $\Delta m/z = 0.654$ ppm; UV/VIS (CH₂Cl₂) $\lambda_{\max}$ (ϵ) [nm (l*mol⁻¹*cm⁻¹)] = 277 (865184), 319 (765080), 381 (779381), 652 (2045), 606 (315); Elemental Analysis calcd. for C₃₅H₃₃AuClFN₂O₂: C: 54.95, H: 4.35, N : 3.66, found C: 54.49, H: 4.81, N: 3.07.

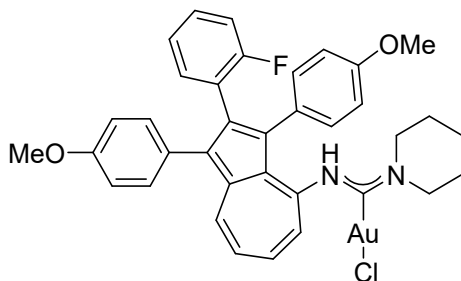
Synthesis of (((2-(2-fluorophenyl)-1,3-bis(4-methoxyphenyl)azulen-4-yl)amino)(pyrrolidin-1-yl)methyl)gold(I) chloride (14ab)



According to **GP1** 2-(2-fluorophenyl)-4-isocyano-1,3-bis(4-methoxyphenyl)azulene gold(I)chloride (**12a**) (50.0 mg, 72.3 μ mol, 1.00 eq.) and pyrrolidine (**13b**) (5.40 mg, 75.9 μ mol, 1.05 eq.) was stirred in dichloromethane at room temperature 12 hours. Purification by flash column chromatography (Silica, dichloromethane) yielded the title compound as a blue solid (36.0 mg, 47.2 μ mol, 65%).

MP = 213 – 218 °C; **$^1\text{H}\{^{19}\text{F}\}$ NMR** (301 MHz, C_6D_6 , 295 K) δ [ppm] = 8.33 (dd, J = 9.7, 1.2 Hz, 1H, C_{ArH}), 8.13 (d, J = 10.6 Hz, 1H, NH), 7.35 (d, J = 8.5 Hz, 2H, $2\times\text{C}_{\text{ArH}}$), 7.32 – 7.27 (m, 1H, C_{ArH}), 7.08 – 6.98 (m, 3H, $3\times\text{C}_{\text{ArH}}$), 6.93 (dd, J = 8.4, 2.2 Hz, 1H, C_{ArH}), 6.80 (d, J = 8.9 Hz, 2H, $2\times\text{C}_{\text{ArH}}$), 6.76 – 6.62 (m, 4H, $4\times\text{C}_{\text{ArH}}$), 6.44 (ddd, J = 16.8, 8.5, 2.8 Hz, 2H, $2\times\text{C}_{\text{ArH}}$), 3.75 – 3.42 (m, 2H, $-\text{CH}_2-$), 3.30 (s, 3H, $-\text{OCH}_3$), 3.15 (s, 3H, $-\text{OCH}_3$), 1.64 – 1.42 (m, 1H, $-\text{CH}_2-$), 1.30 (q, J = 5.4 Hz, 1H, $-\text{CH}_2-$), 1.19 – 1.02 (m, 4H, $2\times\text{CH}_2-$); **$^{13}\text{C}\{^{19}\text{F}, ^1\text{H}\}$ NMR** (176 MHz, C_6D_6 , 295 K) δ [ppm] = 189.84 (s, 1C, $\text{C}_{\text{Carbene}}$), 160.03 (s, 1C, C_{Ar}), 159.32 (s, 1C, C_{Ar}), 158.81 (s, 1C, C_{Ar}), 146.37 (s, 1C, C_{Ar}), 143.52 (s, 1C, C_{Ar}), 138.95 (s, 1C, C_{Ar}), 137.56 (d, 1C, C_{ArH}), 136.86 (d, 1C, C_{ArH}), 134.71 (d, 1C, C_{ArH}), 133.25 (d, 1C, C_{ArH}), 133.10 (d, 1C, C_{ArH}), 132.58 (d, 1C, C_{ArH}), 132.43 (s, 1C, C_{Ar}), 129.62 (s, 1C, C_{Ar}), 129.30 (d, 1C, C_{ArH}), 129.25 (d, 1C, C_{ArH}), 127.30 (s, 1C, C_{Ar}), 126.60 (s, 1C, C_{Ar}), 125.74 (s, 1C, C_{Ar}), 125.66 (s, 1C, C_{Ar}), 123.77 (d, 1C, C_{ArH}), 123.57 (d, 1C, C_{ArH}), 122.78 (d, 1C, C_{ArH}), 115.63 (d, 1C, C_{ArH}), 115.59 (d, 1C, C_{ArH}), 114.22 (d, 1C, C_{ArH}), 113.13 (d, 1C, C_{ArH}), 113.01 (d, 1C, C_{ArH}), 56.34 (t, 1C, $-\text{CH}_2-$), 54.78 (q, 1C, $-\text{OCH}_3$), 54.71 (q, 1C, $-\text{OCH}_3$), 44.06 (t, 1C, $-\text{CH}_2-$), 24.75 (t, 1C, $-\text{CH}_2-$), 23.91 (t, 1C, $-\text{CH}_2-$); **$^{19}\text{F}\{^1\text{H}\}$ NMR** (283 MHz, C_6D_6 , 295 K) δ [ppm] = -112.00 (s, 1F, C_{ArF}); **IR** (ATR) $\tilde{\nu}$ [cm^{-1}] = 3319 (m), 2935 (w), 2835 (w), 1708 (s), 1607 (m), 1589 (m), 1538 (s), 1459 (m), 1449 (m), 1364 (w), 1294 (m), 1264 (s), 1224 (s), 1176 (s), 1124 (s), 1108 (s), 950 (w), 929 (w), 825 (w), 775 (w), 728 (w), 638 (w); **HR-MS** (MALDI): $\text{C}_{35}\text{H}_{31}\text{AuClFN}_2\text{O}_2$ $[\text{M}]^+$ calcd.: 762.1724, found.: 762.1729, $\Delta m/z$ = 0.656 ppm; **UV/VIS** (CH_2Cl_2) λ_{max} (ϵ) [nm ($\text{l}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$)] = 277 (37270), 321 (37270), 380 (7043), 608 (704); **Elemental Analysis** calcd. for $\text{C}_{35}\text{H}_{31}\text{AuClFN}_2\text{O}_2$: C: 55.09, H: 4.10, N : 3.67, found C: 55.05, H: 4.33, N: 3.58.

Synthesis of (((2-(2-fluorophenyl)-1,3-bis(4-methoxyphenyl)azulen-4-yl)amino)(piperidin-1-yl)methylene)gold(I) chloride (14ac)



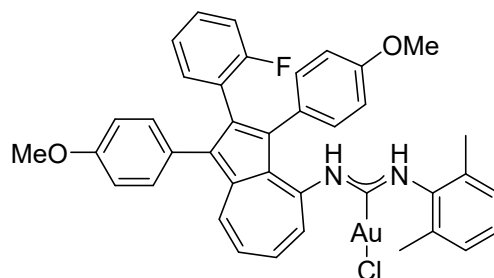
According to **GP1** 2-(2-fluorophenyl)-4-isocyano-1,3-bis(4-methoxyphenyl)azulene gold(I)chloride (**12a**) (50.0 mg, 72.3 μmol , 1.00eq.) and piperidine (**13c**) (6.46 mg, 75.9 μmol , 1.05 eq.) was stirred in dichloromethane at room temperature 12 hours. Purification by flash

column chromatography (Silica, dichloromethane) yielded the title compound as a blue solid (38.0 mg, 48.9 μ mol, 68%).

According to **GP2** [AuCl(DMS)] (52.6 mg, 179 μ mol, 1.00 eq.) and 2-(2-fluorophenyl)-4-isocyano-1,3-bis(4-methoxyphenyl)azulene (82.0 mg, 178 μ mol, 1.00 eq.) were stirred in dichloromethane for 1 hour at room temperature. Afterwards, piperidine (16.0 mg, 187 μ mol, 1.05 eq.) was added, the mixture stirred at room temperature for additional 12 hours. Purification by flash column chromatography (Silica, dichloromethane) yielded the title compound as a blue solid (90.0 mg, 116 μ mol, 65%).

MP = 164 – 169 °C; **$^1\text{H}\{^{19}\text{F}\}$ NMR** (600 MHz, C_6D_6 , 295 K) δ [ppm] = 8.32 (dd, J = 9.6, 1.2 Hz, 1H, NH), 7.91 (d, J = 10.5 Hz, 1H, C_{ArH}), 7.36 (d, J = 8.0 Hz, 1H, C_{ArH}), 7.26 (ddd, J = 10.7, 9.8, 1.2 Hz, 1H, C_{ArH}), 7.05 (s, 1H, C_{ArH}), 7.03 – 6.97 (m, 2H, $2\times\text{C}_{\text{ArH}}$), 6.91 (dd, J = 8.4, 2.3 Hz, 1H, C_{ArH}), 6.82 – 6.78 (m, 2H, $2\times\text{C}_{\text{ArH}}$), 6.78 – 6.71 (m, 2H, $2\times\text{C}_{\text{ArH}}$), 6.69 (td, J = 9.6, 0.7 Hz, 1H, C_{ArH}), 6.67 – 6.63 (m, 1H, C_{ArH}), 6.43 (dd, J = 8.4, 2.8 Hz, 1H, C_{ArH}), 6.39 (dd, J = 8.4, 2.9 Hz, 1H, C_{ArH}), 4.01 – 3.82 (m, 1H, $-\text{CH}_2-$), 3.64 (ddd, J = 13.1, 7.2, 4.6 Hz, 1H, $-\text{CH}_2-$), 3.28 (s, 3H, $-\text{OCH}_3$), 3.14 (s, 3H, $-\text{OCH}_3$), 1.78 (ddd, J = 13.3, 7.0, 4.0 Hz, 1H, $-\text{CH}_2-$), 1.64 (ddd, J = 12.9, 7.8, 4.1 Hz, 1H, $-\text{CH}_2-$), 1.06 (dp, J = 7.4, 3.1 Hz, 2H, $-\text{CH}_2-$), 0.95 – 0.82 (m, 2H, $-\text{CH}_2-$), 0.55 (dddd, J = 14.2, 11.3, 7.5, 4.2 Hz, 2H, $-\text{CH}_2-$); **$^{13}\text{C}\{^{19}\text{F}, ^1\text{H}\}$ NMR** (151 MHz, C_6D_6 , 295 K) δ [ppm] = 190.88 (s, 1C, $\text{C}_{\text{Carbene}}$), 161.56 (s, 1C, C_{Ar}), 159.92 (s, 1C, C_{Ar}), 159.23 (s, 1C, C_{Ar}), 158.86 (s, 1C, C_{Ar}), 146.23 (s, 1C, C_{Ar}), 143.47 (s, 1C, C_{Ar}), 138.87 (s, 1C, C_{Ar}), 137.50 (s, 1C, C_{Ar}), 136.68 (d, 1C, C_{ArH}), 134.73 (d, 1C, C_{ArH}), 133.05 (d, 1C, C_{ArH}), 132.60 (d, 1C, C_{ArH}), 132.30 (s, 1C, C_{Ar}), 129.29 (d, 1C, C_{ArH}), 129.25 (d, 1C, C_{ArH}), 127.61 (s, 1C, C_{Ar}), 127.41 (s, 1C, C_{Ar}), 126.65 (d, 1C, C_{ArH}), 125.77 (s, 1C, C_{Ar}), 123.80 (d, 1C, C_{ArH}), 123.78 (d, 1C, C_{ArH}), 123.58 (d, 1C, C_{ArH}), 122.74 (d, 1C, C_{ArH}), 115.70 (d, 1C, C_{ArH}), 115.55 (d, 1C, C_{ArH}), 114.21 (d, 1C, C_{ArH}), 113.51 (d, 1C, C_{ArH}), 113.05 (d, 1C, C_{ArH}), 58.28 (t, 1C, $-\text{CH}_2-$), 54.83 (q, 1C, $-\text{OCH}_3$), 54.71 (q, 1C, $-\text{OCH}_3$), 44.66 (t, 1C, $-\text{CH}_2-$), 25.83 (t, 1C, $-\text{CH}_2-$), 24.81 (t, 1C, $-\text{CH}_2-$), 23.55 (t, 1C, $-\text{CH}_2-$); **$^{19}\text{F}\{^1\text{H}\}$ NMR** (283 MHz, C_6D_6 , 295 K) δ [ppm] = -112.17; **IR** (ATR) $\tilde{\nu}$ [cm^{-1}] = 3318, 2930, 2853, 2836, 1607, 1568, 1538, 1515, 1480, 1450, 1353, 1318, 1284, 1243, 1175, 1105, 1029, 950, 834, 807, 753, 729, 634; **HR-MS** (MALDI): $\text{C}_{36}\text{H}_{33}\text{AuClFN}_2\text{O}_2$ $[\text{M}]^+$ calcd.: 776.1880, found.: 776.1875, $\Delta m/z$ = 0.644 ppm; **UV/VIS** (CH_2Cl_2) λ_{max} (ϵ) [nm ($\text{l}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$)] = 278 (53730), 323 (47514), 381 (48402), 607 (1270); **Elemental Analysis** calcd. for $\text{C}_{36}\text{H}_{33}\text{AuClFN}_2\text{O}_2$: C: 55.64, H: 4.28, N: 3.61, found C: 55.68, H: 4.59, N: 3.57.

Synthesis of (((2,6-dimethylphenyl)amino)((2-(2-fluorophenyl)-1,3-bis(4-methoxyphenyl)azulen-4-yl)amino)methylene)gold(III) chloride (14ad)

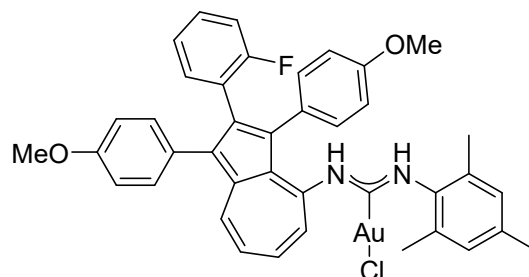


According to **GP1** 2-(2-fluorophenyl)-4-isocyano-1,3-bis(4-methoxyphenyl)azulene gold(I)chloride (**12a**) (50.0 mg, 72.3 μmol , 1.00 eq.) and 2,6-dimethylaniline (**13d**) (9.19 mg, 75.9 μmol , 1.05 eq.) was stirred in dichloromethane at room temperature 12 hours. Purification by flash column chromatography (Silica, dichloromethane) yielded the title compound as a blue solid (36.0 mg, 44.3 μmol , 62%).

MP = 222 – 227 °C; **$^1\text{H}\{^{19}\text{F}\}$ NMR** (301 MHz, C_6D_6 , 295 K) δ [ppm] = 10.28 (s, 1H, NH), 8.31 – 8.28 (m, 1H, NH), 8.27 (d, J = 2.5 Hz, 1H, C_{ArH}), 8.14 (s, 1H, C_{ArH}), 7.37 – 7.29 (m, 1H, C_{ArH}), 7.26 (d, J = 8.8 Hz, 2H, $2\times\text{C}_{\text{ArH}}$), 6.91 (d, J = 7.6 Hz, 1H, C_{ArH}), 6.84 (td, J = 7.4, 1.8 Hz, 2H, $2\times\text{C}_{\text{ArH}}$), 6.74 (s, 1H, C_{ArH}), 6.71 (s, 2H, $2\times\text{C}_{\text{ArH}}$), 6.69 (s, 1H, C_{ArH}), 6.65 (s, 1H, C_{ArH}), 6.63 (s, 1H, C_{ArH}), 6.60 (d, J = 1.8 Hz, 1H, C_{ArH}), 6.57 (s, 1H, C_{ArH}), 6.54 (dd, J = 7.2, 1.6 Hz, 1H, C_{ArH}), 6.20 (dd, J = 8.3, 2.8 Hz, 1H, C_{ArH}), 6.11 (dd, J = 8.4, 2.9 Hz, 1H, C_{ArH}), 3.24 (s, 3H, $-\text{OCH}_3$), 3.15 (s, 3H, $-\text{OCH}_3$), 1.93 (s, 3H, $-\text{CH}_3$), 1.87 (s, 3H, $-\text{CH}_3$); **$^{13}\text{C}\{^{19}\text{F}, ^1\text{H}\}$ NMR** (176 MHz, C_6D_6 , 295 K) δ [ppm] = 188.81 (s, 1C, $\text{C}_{\text{Carbene}}$), 161.22 (s, 1C, C_{Ar}), 159.80 (s, 1C, C_{Ar}), 159.13 (s, 1C, C_{Ar}), 158.33 (s, 1C, C_{Ar}), 146.15 (s, 1C, C_{Ar}), 144.40 (s, 1C, C_{Ar}), 143.30 (s, 1C, C_{Ar}), 138.88 (s, 1C, C_{Ar}), 137.49 (d, 1C, C_{ArH}), 136.45 (d, 1C, C_{ArH}), 134.32 (s, 1C, C_{Ar}), 134.11 (s, 1C, C_{Ar}), 132.73 (d, 1C, C_{ArH}), 132.57 (d, 1C, C_{ArH}), 132.44 (s, 1C, C_{Ar}), 131.84 (d, 1C, C_{Ar}), 131.59 (d, 1C, C_{ArH}), 129.28 (d, 1C, C_{ArH}), 128.59 (d, 1C, C_{ArH}), 128.35 (d, 1C, C_{ArH}), 128.31 (s, 1C, C_{Ar}), 125.60 (s, 1C, C_{Ar}), 125.49 (s, 1C, C_{Ar}), 125.21 (s, 1C, C_{Ar}), 123.42 (d, 1C, C_{ArH}), 121.60 (d, 1C, C_{ArH}), 121.40 (d, 1C, C_{ArH}), 118.18 (d, 1C, C_{ArH}), 115.40 (d, 1C, C_{ArH}), 115.28 (d, 1C, C_{ArH}), 114.10 (d, 1C, C_{ArH}), 113.96 (d, 1C, C_{ArH}), 113.84 (d, 1C, C_{ArH}), 113.63 (d, 1C, C_{ArH}), 54.67 (q, 1C, $-\text{OCH}_3$), 54.35 (q, 1C, $-\text{OCH}_3$), 19.07 (q, 1C, $-\text{CH}_3$), 19.00 (q, 1C, $-\text{CH}_3$); **$^{19}\text{F}\{^1\text{H}\}$ NMR** (283 MHz, C_6D_6 , 295 K) δ [ppm] = -111.85 (s, 1F, C_{ArF}); **IR** (ATR) $\tilde{\nu}$ [cm^{-1}] = 3259 (m), 3204 (m), 2965 (w), 2834 (w), 1607 (m), 1569 (m), 1515 (s), 1473 (m), 1449 (m), 1386 (w), 1264 (s), 1224 (s), 1175 (s), 1107 (s), 1030 (s), 831 (w), 753 (w), 739 (w), 617 (w); **HR-MS** (MALDI): $\text{C}_{39}\text{H}_{33}\text{AuClFN}_2\text{O}_2$ $[\text{M}]^+$ calcd.: 812.1880, found.: 812.1879, $\Delta m/z$ = 0.123 ppm; **UV/VIS** (CH_2Cl_2) λ_{max} (ϵ) [nm ($\text{l}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$)] = 279 (23461),

321 (23461), 385 (3871), 613 (607); **Elemental Analysis** calcd. for $C_{39}H_{33}AuClFN_2O_2$: C: 57.61, H: 4.09, N : 3.45, found C: 57.04, H: 4.03, N: 3.42.

Synthesis of (((2-(2-fluorophenyl)-1,3-bis(4-methoxyphenyl)azulen-4-yl)amino)(mesitylamino)methylene)gold(I) chloride (14ae)

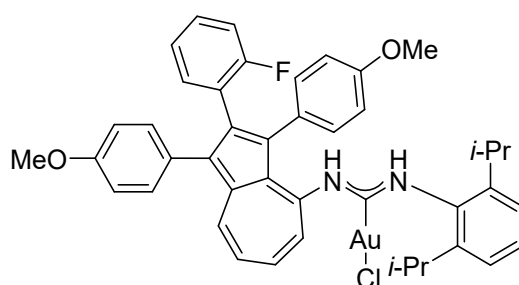


According to **GP1** 2-(2-fluorophenyl)-4-isocyano-1,3-bis(4-methoxyphenyl)azulene gold(I)chloride (**12a**) (50.0 mg, 72.3 μ mol, 1.00 eq.) and mesitylamine (**13e**) (10.2 mg, 75.9 μ mol, 1.05 eq.) was stirred in dichloromethane at room temperature 12 hours. Purification by flash column chromatography (Silica, dichloromethane) yielded the title compound as a blue solid (39.0 mg, 47.2 μ mol, 65%).

MP = 177 – 182 °C; **$^1H\{^{19}F\}$ NMR** (500 MHz, C_6D_6 , 295 K) δ [ppm] = 10.08 (s, 1H, NH), 8.16 (d, J = 10.6 Hz, 1H, $C_{Ar}H$), 8.11 (dd, J = 9.6, 1.3 Hz, 1H, $C_{Ar}H$), 7.99 (s, 1H, NH), 7.16 (ddd, J = 10.9, 9.9, 1.3 Hz, 1H, $C_{Ar}H$), 7.09 (d, J = 8.8 Hz, 2H, $2 \times C_{Ar}H$), 6.67 (td, J = 7.4, 1.8 Hz, 1H, $C_{Ar}H$), 6.60 (dd, J = 8.5, 2.4 Hz, 1H, $C_{Ar}H$), 6.56 (d, J = 8.9 Hz, 2H, $2 \times C_{Ar}H$), 6.54 – 6.51 (m, 1H, $C_{Ar}H$), 6.50 (d, J = 9.7 Hz, 1H, $C_{Ar}H$), 6.46 (ddd, J = 8.8, 5.3, 1.6 Hz, 1H, $C_{Ar}H$), 6.42 (dd, J = 9.4, 1.3 Hz, 1H, $C_{Ar}H$), 6.38 (td, J = 7.3, 1.3 Hz, 1H, $C_{Ar}H$), 6.26 (d, J = 12.2 Hz, 2H, $2 \times C_{Ar}H$), 6.03 (dd, J = 8.4, 2.8 Hz, 1H, $C_{Ar}H$), 5.95 (dd, J = 8.5, 2.7 Hz, 1H, $C_{Ar}H$), 3.07 (s, 3H, -OCH₃), 2.99 (s, 3H, -OCH₃), 1.78 (s, 3H, -CH₃), 1.75 (s, 3H, -CH₃), 1.69 (s, 3H, -CH₃); **$^{13}C\{^{19}F, ^1H\}$ NMR** (101 MHz, C_6D_6 , 295 K) δ [ppm] = 188.94 (s, 1C, $C_{Carbene}$), 161.78 (s, 1C, C_{Ar}), 159.33 (s, 1C, C_{Ar}), 159.15 (s, 1C, C_{Ar}), 158.49 (s, 1C, C_{Ar}), 146.32 (s, 1C, C_{Ar}), 144.35 (s, 1C, C_{Ar}), 138.91 (s, 1C, C_{Ar}), 137.70 (s, 1C, C_{Ar}), 137.46 (d, 1C, $C_{Ar}H$), 136.46 (d, 1C, $C_{Ar}H$), 133.97 (s, 1C, C_{Ar}), 133.80 (s, 1C, C_{Ar}), 132.81 (d, 1C, $C_{Ar}H$), 132.78 (d, 1C, $C_{Ar}H$), 132.59 (d, 1C, $C_{Ar}H$), 132.44 (s, 1C, C_{Ar}), 131.92 (d, 1C, $C_{Ar}H$), 131.73 (d, 1C, $C_{Ar}H$), 130.44 (s, 1C, C_{Ar}), 130.02 (d, 1C, $C_{Ar}H$), 129.03 (d, 1C, $C_{Ar}H$), 128.70 (s, 1C, C_{Ar}), 128.51 (s, 1C, C_{Ar}), 125.73 (s, 1C, C_{Ar}), 125.56 (s, 1C, C_{Ar}), 125.16 (d, 1C, $C_{Ar}H$), 123.43 (d, 1C, $C_{Ar}H$), 123.16 (d, 1C, $C_{Ar}H$), 121.62 (d, 1C, $C_{Ar}H$), 115.45 (d, 1C, $C_{Ar}H$), 115.23 (d, 1C, $C_{Ar}H$), 114.10 (d, 1C, $C_{Ar}H$), 113.73 (d, 1C, $C_{Ar}H$), 113.44 (d, 1C, $C_{Ar}H$), 54.68 (q, 1C, -OCH₃), 54.40 (q, 1C, -OCH₃), 20.84 (q, 1C, -CH₃), 19.01 (q, 1C, -CH₃), 18.95 (q, 1C, -CH₃); **$^{19}F\{^1H\}$ NMR** (471

MHz, C₆D₆, 295 K) δ [ppm] = -111.80 (s, 1F, C_{Ar}F); **IR** (ATR) $\tilde{\nu}$ [cm⁻¹] = 3263 (m), 3205 (m), 2965 (w), 2934 (w), 1708 (s), 1608 (m), 1569 (m), 1516 (s), 1475 (m), 1449 (m), 1384 (w), 1264 (s), 1224 (s), 1175 (s), 1107 (s), 1030 (s), 829 (w), 754 (w), 729 (w), 619 (w); **HR-MS** (MALDI): C₄₀H₃₅AuClFN₂O₂ [M]⁺ calcd.: 826.2037, found.: 826.2033, $\Delta m/z$ = 0.484 ppm; **UV/VIS** (CH₂Cl₂) $\lambda_{\max}$ (ϵ) [nm (l*mol⁻¹*cm⁻¹)] = 281 (42780), 322 (43049), 614 (615); **Elemental Analysis** calcd. for C₄₀H₃₅AuClFN₂O₂: C: 58.08, H: 4.27, N : 3.39, found C: 58.95, H: 4.93, N: 3.40.

Synthesis of (((2,6-diisopropylphenyl)amino)((2-(2-fluorophenyl)-1,3-bis(4-methoxyphenyl)azulen-4-yl)amino)methylene)gold(I) chloride (14af)



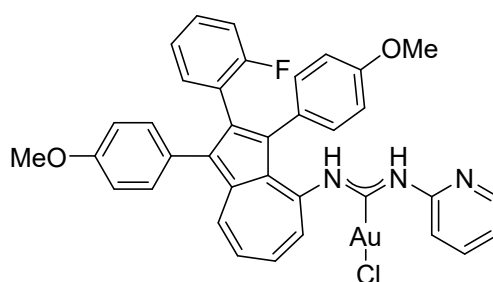
According to **GP1** 2-(2-fluorophenyl)-4-isocyano-1,3-bis(4-methoxyphenyl)azulene gold(I)chloride (**12a**) (50.0 mg, 72.3 μ mol, 1.00 eq.) and 2,6-diisopropylaniline (**13f**) (13.5 mg, 75.9 μ mol, 1.05 eq.) was stirred in dichloromethane at room temperature 12 hours. Purification by flash column chromatography (Silica, dichloromethane) yielded the title compound as a blue solid (33.0 mg, 38.0 μ mol, 52%).

According to **GP2** [AuCl(DMS)] (**11**) (52.6 mg, 179 μ mol, 1.00 eq.) and 2-(2-fluorophenyl)-4-isocyano-1,3-bis(4-methoxyphenyl)azulene (**10a**) (82.0 mg, 178 μ mol, 1.00 eq.) were stirred in dichloromethane for 1 hour at room temperature. Afterwards, 2,6-diisopropylaniline (**13f**) (47.5 mg, 268 μ mol, 1.05 eq.) was added, the mixture stirred at room temperature for additional 12 hours. Purification by flash column chromatography (Silica, dichloromethane) yielded the title compound as a blue solid (68.0 mg, 87.5 μ mol, 49%).

MP = 169 – 174 °C; **¹H{¹⁹F} NMR** (500 MHz, C₆D₆, 295 K) δ [ppm] = 10.10 (s, 1H, NH), 8.33 (s, 1H, NH), 8.02 (dd, J = 9.4, 1.2 Hz, 1H, C_{Ar}H), 7.79 (d, J = 10.6 Hz, 1H, C_{Ar}H), 7.11 – 7.06 (m, 2H, 2xC_{Ar}H), 7.01 (d, J = 8.8 Hz, 2H, 2xC_{Ar}H), 6.87 (dd, J = 7.4, 1.8 Hz, 1H, C_{Ar}H), 6.81 (t, J = 7.8 Hz, 1H, C_{Ar}H), 6.76 (s, 1H, C_{Ar}H), 6.68 (dd, J = 7.5, 1.9 Hz, 1H, C_{Ar}H), 6.63 – 6.58 (m, 2H, 2xC_{Ar}H), 6.55 – 6.52 (m, 2H, 2xC_{Ar}H), 6.50 (dd, J = 2.9, 1.2 Hz, 1H, C_{Ar}H), 6.49 – 6.46 (m, 1H, C_{Ar}H), 6.45 – 6.36 (m, 2H, 2xC_{Ar}H), 5.96 (d, J = 8.8 Hz, 1H, C_{Ar}H), 3.03 (s, 3H, -OCH₃), 2.97 (s, 3H, -OCH₃), 2.82 (p, J = 6.8 Hz, 1H, -CH(CH₃)₂), 2.73 (p, J = 6.8 Hz, 1H, -

CH(CH₃)₂), 0.77 (d, *J* = 6.9 Hz, 3H, -CH(CH₃)₂), 0.76 – 0.71 (m, 6H, 2x-CH(CH₃)₂), 0.70 (d, *J* = 6.9 Hz, 3H, -CH(CH₃)₂); ¹³C{¹⁹F, ¹H} NMR (126 MHz, C₆D₆, 295 K) δ [ppm] = 191.50 (s, 1C, C_{Carbene}), 159.49 (s, 1C, C_{Ar}), 157.91 (s, 1C, C_{Ar}), 157.01 (s, 1C, C_{Ar}), 145.90 (s, 1C, C_{Ar}), 143.99 (s, 1C, C_{Ar}), 143.95 (s, 1C, C_{Ar}), 143.20 (s, 1C, C_{Ar}), 139.21 (s, 1C, C_{Ar}), 135.79 (d, 1C, C_{Ar}H), 134.92 (d, 1C, C_{Ar}H), 133.27 (s, 1C, C_{Ar}), 131.63 (d, 1C, C_{Ar}H), 131.47 (d, 1C, C_{Ar}H), 131.34 (d, 1C, C_{Ar}H), 130.53 (s, 1C, C_{Ar}), 130.43 (d, 1C, C_{Ar}H), 129.98 (s, 1C, C_{Ar}), 129.56 (s, 1C, C_{Ar}), 128.74 (d, 1C, C_{Ar}H), 127.91 (d, 1C, C_{Ar}H), 127.39 (d, 1C, C_{Ar}H), 127.35 (d, 1C, C_{Ar}H), 126.21 (d, 1C, C_{Ar}H), 124.56 (s, 1C, C_{Ar}), 123.47 (d, 1C, C_{Ar}H), 123.35 (d, 1C, C_{Ar}H), 123.28 (s, 1C, C_{Ar}), 122.59 (d, 1C, C_{Ar}H), 122.38 (d, 1C, C_{Ar}H), 121.69 (s, 1C, C_{Ar}), 114.26 (d, 1C, C_{Ar}H), 113.35 (d, 1C, C_{Ar}H), 113.01 (d, 1C, C_{Ar}H), 112.86 (d, 1C, C_{Ar}H), 53.46 (q, 1C, -OCH₃), 52.99 (q, 1C, -OCH₃), 27.97 (d, 1C, -CH(CH₃)₂), 27.92 (d, 1C, -CH(CH₃)₂), 23.83 (q, 1C, -CH(CH₃)₂), 23.78 (q, 1C, -CH(CH₃)₂), 21.58 (q, 1C, -CH(CH₃)₂), 21.52 (q, 1C, -CH(CH₃)₂); ¹⁹F{¹H} NMR (471 MHz, C₆D₆, 295 K) δ [ppm] = -112.15 (s, 1F, C_{Ar}F); IR (ATR) $\tilde{\nu}$ [cm⁻¹] = 3270 (m), 2981 (w), 2929 (w), 2867 (w), 2835 (w), 1609 (m), 1589 (m), 1520 (s), 1450 (m), 1384 (w), 1266 (s), 1214 (s), 1176 (s), 1106 (s), 1031 (s), 933 (w), 831 (w), 725 (w), 728 (w); HR-MS (MALDI): C₄₃H₄₁AuClFN₂O₂ [M]⁺ calcd.: 868.2506, found.: 868.2504, Δ*m/z* = 0.230 ppm; UV/VIS (CH₂Cl₂) λ_{max} (ε) [nm (l*mol⁻¹*cm⁻¹)] = 276 (42104), 319 (44631), 384 (9004), 618 (593); Elemental Analysis calcd. for C₄₃H₄₁AuClFN₂O₂: C: 59.42, H: 4.75, N : 3.22, found C: 59.90, H: 5.21, N: 3.21.

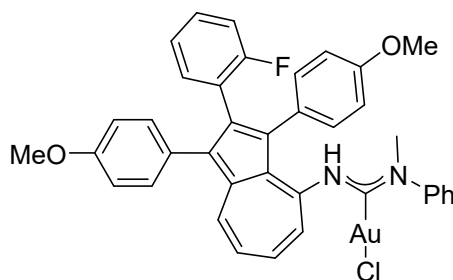
Synthesis of (((2-(2-fluorophenyl)-1,3-bis(4-methoxyphenyl)azulen-4-yl)amino)(pyridin-2-ylamino)methylene)gold(I) chloride (14ag)



According to **GP1** 2-(2-fluorophenyl)-4-isocyano-1,3-bis(4-methoxyphenyl)azulene gold(I)chloride (**12a**) (50.0 mg, 72.3 μmol, 1.00 eq.) and pyridine-2-amine (**13g**) (7.14 mg, 75.9 μmol, 1.05 eq.) was stirred in dichloromethane at room temperature 12 hours. Purification by flash column chromatography (Silica, dichloromethane) yielded the title compound as a blue solid (36.0 mg, 48.8 μmol, 63%).

MP = 234 – 239 °C; **$^1\text{H}\{^{19}\text{F}\}$ NMR** (301 MHz, CD_2Cl_2 , 295 K) δ [ppm] = 13.82 (s, 1H, NH), 9.70 (s, 1H, NH), 8.28 (d, J = 9.5 Hz, 1H, $\text{C}_{\text{Ar}}\text{H}$), 7.69 (d, J = 4.3 Hz, 1H, $\text{C}_{\text{Ar}}\text{H}$), 7.65 – 7.44 (m, 3H, $3\times\text{C}_{\text{Ar}}\text{H}$), 7.19 – 7.03 (m, 5H, $5\times\text{C}_{\text{Ar}}\text{H}$), 6.94 – 6.82 (m, 4H, $4\times\text{C}_{\text{Ar}}\text{H}$), 6.78 (d, J = 6.7 Hz, 4H, $4\times\text{C}_{\text{Ar}}\text{H}$), 6.42 – 6.15 (m, 2H, $2\times\text{C}_{\text{Ar}}\text{H}$), 3.72 (s, 3H, $-\text{OCH}_3$), 3.26 (s, 3H, $-\text{OCH}_3$); **$^{13}\text{C}\{^{19}\text{F}, ^1\text{H}\}$ NMR** (101 MHz, CD_2Cl_2 , 295 K) δ [ppm] = 190.33 (s, 1C, $\text{C}_{\text{Carbene}}$), 158.98 (s, 1C, C_{Ar}), 157.77 (s, 1C, C_{Ar}), 154.23 (s, 1C, C_{Ar}), 146.20 (d, 1C, $\text{C}_{\text{Ar}}\text{H}$), 145.90 (s, 1C, C_{Ar}), 145.03 (s, 1C, C_{Ar}), 139.03 (s, 1C, C_{Ar}), 138.91 (d, 1C, $\text{C}_{\text{Ar}}\text{H}$), 137.21 (d, 1C, $\text{C}_{\text{Ar}}\text{H}$), 136.49 (d, 1C, $\text{C}_{\text{Ar}}\text{H}$), 132.99 (d, 1C, $\text{C}_{\text{Ar}}\text{H}$), 132.96 (d, 1C, $\text{C}_{\text{Ar}}\text{H}$), 132.40 (d, 1C, $\text{C}_{\text{Ar}}\text{H}$), 132.26 (s, 1C, C_{Ar}), 129.59 (s, 1C, C_{Ar}), 129.33 (d, 1C, $\text{C}_{\text{Ar}}\text{H}$), 129.25 (d, 1C, $\text{C}_{\text{Ar}}\text{H}$), 128.66 (s, 1C, C_{Ar}), 128.11 (s, 1C, C_{Ar}), 127.58 (s, 1C, C_{Ar}), 125.37 (s, 1C, C_{Ar}), 125.21 (s, 1C, C_{Ar}), 124.38 (d, 1C, $\text{C}_{\text{Ar}}\text{H}$), 123.83 (d, 1C, $\text{C}_{\text{Ar}}\text{H}$), 123.58 (d, 1C, $\text{C}_{\text{Ar}}\text{H}$), 123.54 (d, 1C, $\text{C}_{\text{Ar}}\text{H}$), 119.86 (d, 1C, $\text{C}_{\text{Ar}}\text{H}$), 115.35 (d, 1C, $\text{C}_{\text{Ar}}\text{H}$), 115.13 (d, 1C, $\text{C}_{\text{Ar}}\text{H}$), 113.77 (d, 1C, $\text{C}_{\text{Ar}}\text{H}$), 113.44 (d, 1C, $\text{C}_{\text{Ar}}\text{H}$), 112.70 (d, 1C, $\text{C}_{\text{Ar}}\text{H}$), 112.47 (d, 1C, $\text{C}_{\text{Ar}}\text{H}$), 55.47 (q, 1C, $-\text{OCH}_3$), 54.87 (q, 1C, $-\text{OCH}_3$); **$^{19}\text{F}\{^1\text{H}\}$ NMR** (471 MHz, CD_2Cl_2 , 295 K) δ [ppm] = -113.45 (s, 1F, $\text{C}_{\text{Ar}}\text{F}$); **IR** (ATR) $\tilde{\nu}$ [cm^{-1}] = 3236 (m), 3132 (m), 3120 (m), 3067 (w), 2965 (w), 2936 (w), 1710 (s), 1685 (m), 1605 (m), 1575 (m), 1457 (m), 1433 (m), 1362 (w), 1294 (m), 1267 (s), 1227 (s), 1174 (s), 1129 (s), 1102 (s), 1062 (s), 1028 (s), 882 (w), 828 (w), 788 (w), 730 (w), 682 (w), 624 (w); **HR-MS** (MALDI): $\text{C}_{36}\text{H}_{28}\text{AuClFN}_2\text{O}_2$ $[\text{M}]^+$ calcd.: 785.1520, found.: 785.1517, $\Delta m/z$ = 0.382 ppm; **UV/VIS** (CH_2Cl_2) λ_{max} (ϵ) [nm ($1 \times \text{mol}^{-1} \times \text{cm}^{-1}$)] = 263 (39406), 288 (45894), 319 (36926), 619 (696), 654 (661), 732 (276); **Elemental Analysis** calcd. for $\text{C}_{36}\text{H}_{28}\text{AuClFN}_2\text{O}_2$: C: 55.01, H: 3.59, N : 5.35, found C: 55.59, H: 3.83, N: 5.31.

Synthesis of (((2-(2-fluorophenyl)-1,3-bis(4-methoxyphenyl)azulen-4-yl)amino)(methyl(phenyl)amino)methylene)gold(I) chloride (14ah)

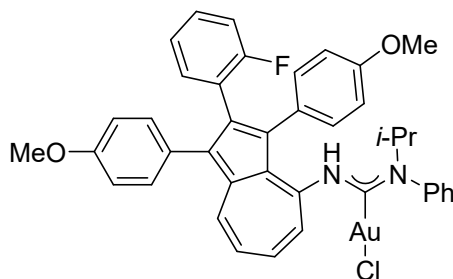


According to **GP1** 2-(2-fluorophenyl)-4-isocyano-1,3-bis(4-methoxyphenyl)azulene gold(I)chloride (**12a**) (50.0 mg, 72.3 μmol , 1.00 eq.) and *N*-methylaniline (**13h**) (8.13 mg, 75.9 μmol , 1.05 eq.) was stirred in dichloromethane at room temperature 12 hours. Purification by flash column chromatography (Silica, dichloromethane) yielded the title compound as a blue solid (41.0 mg, 51.3 μmol , 71%).

MP = 184 – 189 °C; Mixture of Rotamers :Rotamer A : Rotamer B = 1.19 : 1; **¹H{¹⁹F} NMR** (500 MHz, C₆D₆, 295 K) δ [ppm] = 8.13 (dd, J = 9.6, 1.0 Hz, 1H, NH, Rotamer B), 8.01 (dd, J = 9.6, 1.1 Hz, 1H, NH, Rotamer A), 7.90 (d, J = 10.5 Hz, 1H, C_{Ar}H, Rotamer B), 7.57 (d, J = 10.5 Hz, 1H, C_{Ar}H, Rotamer A), 7.16 (d, J = 8.1 Hz, C_{Ar}H, Rotamer A and Rotamer B), 7.09 (d, J = 3.3 Hz, 1H, C_{Ar}H, Rotamer B), 7.06 (d, J = 12.9 Hz, 2H, 2xC_{Ar}H, Rotamer A), 7.04 – 7.01 (m, 1H, C_{Ar}H, Rotamer B), 7.00 (s, 1H, C_{Ar}H, Rotamer B), 6.99 (s, 1H; C_{Ar}H, Rotamer A), 6.88 (d, J = 11.3 Hz, 3H, 3xC_{Ar}H Rotamer A), 6.84 (d, J = 7.9 Hz, 1H, C_{Ar}H Rotamer B), 6.83 – 6.77 (m, 2H, 2xC_{Ar}H, Rotamer A und B), 6.71 (dd, J = 8.4, 2.3 Hz, 1H, C_{Ar}H, Rotamer B), 6.63 – 6.58 (m, 4H, 4xC_{Ar}H, Rotamer A), 6.55 (td, J = 7.6, 1.4 Hz, 6H, 6xC_{Ar}H, Rotamer B), 6.52 – 6.51 (m, 1H, C_{Ar}H, Rotamer A), 6.51 – 6.48 (m, 1H, C_{Ar}H, Rotamer A), 6.48 – 6.46 (m, 1H, C_{Ar}H, Rotamer B), 6.46 – 6.44 (m, 2H, 2xC_{Ar}H, Rotamer A), 6.44 – 6.42 (m, 1H, C_{Ar}H, Rotamer B), 6.39 (td, J = 7.4, 1.3 Hz, 1H, C_{Ar}H, Rotamer B), 6.35 (dd, J = 8.4, 2.8 Hz, 1H, C_{Ar}H, Rotamer A), 6.30 (dd, J = 8.5, 2.9 Hz, 1H, C_{Ar}H, Rotamer B), 6.27 (dd, J = 8.5, 2.9 Hz, 1H, C_{Ar}H, Rotamer B), 6.17 (dd, J = 8.5, 2.7 Hz, 1H, C_{Ar}H, Rotamer A), 5.94 (d, J = 7.8 Hz, 1H, C_{Ar}H, Rotamer A and Rotamer B), 3.14 (s, 3H, -CH₃, Rotamer A), 3.08 (s, 3H, -OCH₃, Rotamer B), 3.06 (s, 6H, 2x-OCH₃, Rotamer A), 2.94 (s, 3H, -OCH₃, Rotamer B), 1.57 (s, 3H, -CH₃, Rotamer B); **¹³C{¹⁹F, ¹H} NMR** (101 MHz, C₆D₆, 295 K) δ [ppm] = 194.04 (s, 1C, C_{Carbene}, Rotamer A), 193.68 (s, 1C, C_{Carbene}, Rotamer B), 161.98 (s, 1C, C_{Ar}, Rotamer B), 161.90 (s, 1C, C_{Ar}, Rotamer A), 159.53 (s, 1C, C_{Ar}, Rotamer B), 159.45 (s, 1C, C_{Ar}, Rotamer A), 159.31 (s, 2C, 2xC_{Ar}, Rotamer A), 159.22 (s, 2C, 2xC_{Ar}, Rotamer B), 158.99 (s, 2C, 2xC_{Ar}, Rotamer B), 158.76 (s, 2C, 2xC_{Ar}, Rotamer A), 148.68 (s, 1C, C_{Ar}, Rotamer B), 145.68 (s, 1C, C_{Ar}, Rotamer A), 145.43 (s, 1C, C_{Ar}, Rotamer A), 144.26 (s, 1C, C_{Ar}, Rotamer B), 144.06 (s, 2C, 2xC_{Ar}, Rotamer B), 140.39 (s, 2C, 2xC_{Ar}, Rotamer A), 139.31 (s, 1C, C_{Ar}, Rotamer A), 139.12 (s, 1C, C_{Ar}, Rotamer B), 137.48 (d, 1C, C_{Ar}H, Rotamer B), 137.18 (d, 1C, C_{Ar}H, Rotamer A), 136.69 (d, 1C, C_{Ar}H, Rotamer B), 136.16 (d, 1C, C_{Ar}H, Rotamer A), 134.67 (d, 1C, C_{Ar}H, Rotamer B), 134.50 (d, 1C, C_{Ar}H, Rotamer A), 133.40 (d, 1C, C_{Ar}H, Rotamer A), 133.22 (d, 1C, C_{Ar}H, Rotamer B), 133.10 (d, 1C, C_{Ar}H, Rotamer B), 133.07 (d, 1C, C_{Ar}H, Rotamer B), 133.04 (d, 2C, 2xC_{Ar}H, Rotamer A), 133.00 (d, 2C, 2xC_{Ar}H, Rotamer A), 132.60 (d, 1C, C_{Ar}H, Rotamer A), 132.52 (d, 1C, C_{Ar}H, Rotamer A), 132.45 (s, 1C, C_{Ar}, Rotamer B), 132.38 (s, 1C, C_{Ar}, Rotamer B), 130.35 (d, 2C, C_{Ar}H, Rotamer A), 129.66 (d, 1C, C_{Ar}H, Rotamer B), 129.56 (s, 1C, C_{Ar}, Rotamer A), 129.40 (d, 1C, C_{Ar}H, Rotamer B), 129.32 (d, 1C, C_{Ar}H, Rotamer B), 129.19 (d, 1C, C_{Ar}H, Rotamer A), 129.11 (d, 1C, C_{Ar}H, Rotamer A), 128.81 (s, 1C, C_{Ar}, Rotamer A), 128.59 (d, 2C, 2xC_{Ar}H, Rotamer B), 127.02 (d, 1C, C_{Ar}H, Rotamer B), 126.32 (d, 1C, C_{Ar}H, Rotamer B), 125.68 (d, 1C, C_{Ar}H, Rotamer A), 123.95 (d, 1C, C_{Ar}H, Rotamer B),

123.91 (d, 1C, $\underline{C_{Ar}H}$, Rotamer A), 123.84(d, 1C, $\underline{C_{Ar}H}$, Rotamer A), 123.80 (d, 1C, $\underline{C_{Ar}H}$, Rotamer B), 123.64 (d, 1C, $\underline{C_{Ar}H}$, Rotamer B), 123.38 (d, 1C, $\underline{C_{Ar}H}$, Rotamer A), 115.76 (d, 1C, $\underline{C_{Ar}H}$, Rotamer A), 115.59 (d, 1C, $\underline{C_{Ar}H}$, Rotamer A), 115.54 (d, 1C, $\underline{C_{Ar}H}$, Rotamer B), 115.37 (d, 1C, $\underline{C_{Ar}H}$, Rotamer B), 114.26 (d, 1C, $\underline{C_{Ar}H}$, Rotamer B), 114.16 (d, 1C, $\underline{C_{Ar}H}$, Rotamer A), 113.66 (d, 1C, $\underline{C_{Ar}H}$, Rotamer B), 113.58 (d, 1C, $\underline{C_{Ar}H}$, Rotamer A), 113.40 (d, 1C, $\underline{C_{Ar}H}$, Rotamer B), 113.06 (d, 1C, $\underline{C_{Ar}H}$, Rotamer A), 54.98 (q, 1C, $-\underline{OCH_3}$, Rotamer A), 54.88 (q, 1C, $-\underline{OCH_3}$, Rotamer B), 54.76 (q, 1C, $-\underline{OCH_3}$, Rotamer B), 54.72 (q, 1C, $-\underline{OCH_3}$, Rotamer A), 48.68 (q, 1C, $-\underline{CH_3}$, Rotamer A), 36.56 (q, 1C, $-\underline{CH_3}$, Rotamer B); $^{19}\text{F}\{^1\text{H}\}$ NMR (283 MHz, C_6D_6 , 295 K) δ [ppm] = -112.04 (s, 1F, $\text{C}_{Ar}\underline{F}$, Rotamer B), -112.08 (s, 1F, $\text{C}_{Ar}\underline{F}$, Rotamer A); IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3320 (m), 2929 (w), 2855 (w), 1607 (m), 1539 (s), 1451 (m), 1393 (w), 1334 (m), 1247 (s), 1204 (s), 1149 (s), 1102 (s), 1029 (s), 980 (m), 889 (w), 789 (m), 729 (w), 694 (w), 614 (w); HR-MS (MALDI): $\text{C}_{38}\text{H}_{31}\text{AuClFN}_2\text{O}_2$ $[\text{M}]^+$ calcd.: 798.1724, found.: 798.1727, $\Delta m/z$ = 0.376 ppm; UV/VIS (CH_2Cl_2) λ_{max} (ϵ) [nm ($\text{l}^*\text{mol}^{-1}*\text{cm}^{-1}$)] = 276 (48060), 320 (4950), 385 (7709), 613 (719), 651 (667), 723 (267); Elemental Analysis calcd. for $\text{C}_{38}\text{H}_{31}\text{AuClFN}_2\text{O}_2$: C: 57.12, H: 3.91, N : 3.51, found C: 57.14, H: 4.34, N: 3.35.

Synthesis of (((2-(2-fluorophenyl)-1,3-bis(4-methoxyphenyl)azulen-4-yl)amino)(isopropyl(phenyl)amino)methylene)gold(I) chloride (14ai)

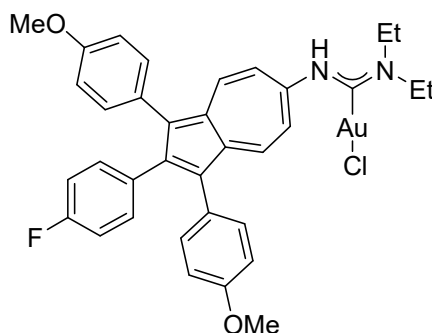


According to **GP1** 2-(2-fluorophenyl)-4-isocyano-1,3-bis(4-methoxyphenyl)azulene gold(I)chloride (**12a**) (50.0 mg, 72.3 μmol , 1.00 eq.) and *N*-isopropylaniline (**13i**) (10.3 mg, 75.9 μmol , 1.05 eq.) was stirred in dichloromethane at room temperature 12 hours. Purification by flash column chromatography (Silica, dichloromethane) yielded the title compound as a blue solid (41.0 mg, 47.2 μmol , 65%).

MP = 210 – 215 $^{\circ}\text{C}$; $^1\text{H}\{^{19}\text{F}\}$ NMR (500 MHz, C_6D_6 , 295 K) δ [ppm] = 8.04 (dd, J = 9.6, 1.1 Hz, 1H, NH), 7.55 (d, J = 10.5 Hz, 1H, $\text{C}_{Ar}\underline{H}$), 7.15 (d, J = 7.9 Hz, 2H, $2\times\text{C}_{Ar}\underline{H}$), 7.06 (d, J = 9.2 Hz, 1H, $\text{C}_{Ar}\underline{H}$), 6.89 (dd, J = 8.5, 2.3 Hz, 1H, $\text{C}_{Ar}\underline{H}$), 6.79 (dd, J = 8.5, 2.4 Hz, 1H, $\text{C}_{Ar}\underline{H}$), 6.68 (dd, J = 7.6, 1.9 Hz, 1H, $\text{C}_{Ar}\underline{H}$), 6.66 – 6.59 (m, 5H, $5\times\text{C}_{Ar}\underline{H}$), 6.60 – 6.55 (m, 3H, $3\times\text{C}_{Ar}\underline{H}$), 6.54 – 6.49 (m, 1H, $\text{C}_{Ar}\underline{H}$), 6.47 (ddt, J = 7.1, 4.6, 2.3 Hz, 3H, $3\times\text{C}_{Ar}\underline{H}$), 6.39 (dd, J = 8.5, 2.7

Hz, 1H, C_{Ar}H), 5.99 (dt, *J* = 6.4, 2.3 Hz, 1H, C_{Ar}H), 5.69 (d, *J* = 7.4 Hz, 1H, C_{Ar}H), 5.51 (p, *J* = 6.8 Hz, 1H, -CH(CH₃)₂), 3.14 (s, 3H, -OCH₃), 3.13 (s, 3H, -OCH₃), 0.69 (d, *J* = 6.8 Hz, 3H, -CH(CH₃)₂), 0.65 (d, *J* = 6.9 Hz, 3H, -CH(CH₃)₂); ¹³C{¹⁹F, ¹H} NMR (101 MHz, C₆D₆, 295 K) δ [ppm] = 194.01 (s, 1C, C_{Carbene}), 161.97 (s, 1C, C_{Ar}), 159.52 (s, 1C, C_{Ar}), 159.22 (s, 1C, C_{Ar}), 158.69 (s, 1C, C_{Ar}), 145.55 (s, 1C, C_{Ar}), 144.36 (s, 1C, C_{Ar}), 139.63 (s, 1C, C_{Ar}), 137.07 (d, 1C, C_{Ar}H), 136.00 (d, 1C, C_{Ar}H), 135.36 (s, 1C, C_{Ar}), 134.92 (d, 1C, C_{Ar}H), 133.88 (d, 1C, C_{Ar}H), 133.10 (d, 1C, C_{Ar}H), 133.06 (d, 1C, C_{Ar}H), 132.51 (d, 1C, C_{Ar}H), 132.34 (s, 1C, C_{Ar}), 130.11 (d, 1C, C_{Ar}H), 130.00 (d, 1C, C_{Ar}H), 129.22 (d, 1C, C_{Ar}H), 129.12 (d, 1C, C_{Ar}H), 129.02 (s, 1C, C_{Ar}), 128.83 (d, 1C, C_{Ar}H), 128.80 (d, 1C, C_{Ar}H), 126.28 (s, 1C, C_{Ar}), 125.88 (s, 1C, C_{Ar}), 125.72 (s, 1C, C_{Ar}), 124.25 (d, 1C, C_{Ar}H), 123.75 (d, 1C, C_{Ar}H), 123.69 (d, 1C, C_{Ar}H), 123.66 (d, 1C, C_{Ar}H), 115.64 (d, 1C, C_{Ar}H), 115.42 (d, 1C, C_{Ar}H), 114.15 (d, 1C, C_{Ar}H), 113.58 (d, 1C, C_{Ar}H), 113.04 (d, 1C, C_{Ar}H), 61.67 (q, 1C, -CH(CH₃)₂), 54.98 (q, 1C, -OCH₃), 54.71 (q, 1C, -OCH₃), 21.59 (q, 1C, -CH(CH₃)₂), 21.29 (q, 1C, -CH(CH₃)₂); ¹⁹F {¹H} NMR (471 MHz, C₆D₆, 295 K) δ [ppm] = -112.04 (s, 1F, C_{Ar}F); IR (ATR) $\tilde{\nu}$ [cm⁻¹] = 3339 (w), 2969 (w), 2930 (w), 1739 (w), 1609 (m), 1558 (s), 1510 (m), 1450 (m), 1347 (w), 1315 (m), 1283 (m), 1244 (s), 1209 (s), 1173 (w), 1108 (m), 1032 (m), 949 (w), 886 (m), 826 (m), 754 (w), 734 (m), 702 (m), 642 (w), 621 (w); HR-MS (MALDI): C₄₈H₃₅AuClFN₂O₂ [M]⁺ calcd.: 826.2037, found.: 826.2038, $\Delta m/z$ = 0.121 ppm; UV/VIS (CH₂Cl₂) $\lambda_{\max}$ (ϵ) [nm (l^{*}mol⁻¹*cm⁻¹)] = 277 (38600), 319 (3885), 383 (6793), 616 (737), 662 (662), 726 (283); Elemental Analysis calcd. for C₄₈H₃₅AuClFN₂O₂: C: 58.08, H: 4.27, N : 3.39, found C: 57.85, H: 4.66, N: 3.24.

Synthesis of ((diethylamino)((2-(4-fluorophenyl)-1,3-bis(4-methoxyphenyl)azulen-6-yl)amino)methylene)gold(I) chloride (14ba)

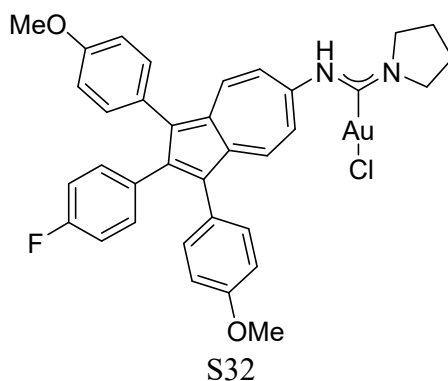


According to **GP1** 2-(4-fluorophenyl)-6-isocyano-1,3-bis(4-methoxyphenyl)azulene gold(I)chloride (**12b**) (50.0 mg, 72.3 μ mol, 1.00 eq.) and diethylamine (**13a**) (5.55 mg, 75.9 μ mol, 1.05 eq.) was stirred in dichloromethane at room temperature 12 hours. Purification by flash column chromatography (Silica, dichloromethane) yielded the title compound as a green solid (49.0 mg, 64.0 μ mol, 88%).

According to **GP2** [AuCl(DMS)] (**11**) (52.6 mg, 178.6 μmol , 1.00 eq.) and 2-(4-fluorophenyl)-6-isocyano-1,3-bis(4-methoxyphenyl)azulene (**10b**) (82.0 mg, 178 μmol , 1.00 eq.) were stirred in dichloromethane for 1 hour at room temperature. Afterwards, diethylamine (**13a**) (13.7 mg, 187 μmol , 1.05 eq.) was added, the mixture stirred at room temperature for additional 12 hours. Purification by flash column chromatography (Silica, dichloromethane) yielded the title compound as a green solid (123 mg, 161 μmol , 90%).

MP = 213 – 218 °C; $^1\text{H}\{^{19}\text{F}\}$ **NMR** (600 MHz, C_6D_6 , 295 K) δ [ppm] = 8.34 (d, J = 11.0 Hz, 2H, $2\times\text{C}_{\text{ArH}}$), 8.06 (s, 1H, NH), 7.27 (d, J = 8.8 Hz, 4H, $4\times\text{C}_{\text{ArH}}$), 7.23 (d, J = 11.0 Hz, 2H, $2\times\text{C}_{\text{ArH}}$), 7.14 – 7.09 (m, 2H, $2\times\text{C}_{\text{ArH}}$), 6.87 (d, J = 8.5 Hz, 4H, $4\times\text{C}_{\text{ArH}}$), 6.71 – 6.63 (m, 2H, $2\times\text{C}_{\text{ArH}}$), 3.38 (s, 6H, $2\times\text{OCH}_3$), 3.38 – 3.33 (m, 2H, $-\text{CH}_2-$), 2.72 (q, J = 7.4 Hz, 2H, $-\text{CH}_2-$), 0.73 (t, J = 7.2 Hz, 3H, $-\text{CH}_3$), 0.59 (t, J = 7.2 Hz, 3H, $-\text{CH}_3$); $^{13}\text{C}\{^{19}\text{F}, ^1\text{H}\}$ **NMR** (151 MHz, C_6D_6 , 295 K) δ [ppm] = 190.67 (s, 1C, $\text{C}_{\text{Carbene}}$), 163.16 (s, 2C, $2\times\text{C}_{\text{Ar}}$), 161.52 (s, 1C, C_{Ar}), 159.16 (s, 2C, $2\times\text{C}_{\text{Ar}}$), 148.68 (s, 1C, C_{Ar}), 146.66 (s, 1C, C_{Ar}), 136.38 (s, 2C, $2\times\text{C}_{\text{Ar}}$), 134.54 (d, 2C, $2\times\text{C}_{\text{ArH}}$), 133.46 (d, 2C, $2\times\text{C}_{\text{ArH}}$), 133.40 (d, 1C, C_{ArH}), 133.23 (d, 2C, $2\times\text{C}_{\text{ArH}}$), 132.93 (d, 1C, C_{ArH}), 130.71 (s, 1C, C_{Ar}), 128.59 (s, 2C, $2\times\text{C}_{\text{Ar}}$), 120.92 (d, 2C, $2\times\text{C}_{\text{ArH}}$), 115.41 (d, 2C, $2\times\text{C}_{\text{ArH}}$), 115.27 (d, 2C, $2\times\text{C}_{\text{ArH}}$), 114.46 (d, 2C, $2\times\text{C}_{\text{ArH}}$), 54.93 (q, 2C, $2\times\text{OCH}_3$), 54.20 (t, 1C, $-\text{CH}_2-$), 42.21 (t, 1C, $-\text{CH}_2-$), 14.40 (q, 1C, $-\text{CH}_3$), 12.21 (q, 1C, $-\text{CH}_3$); $^{19}\text{F}\{^1\text{H}\}$ **NMR** (283 MHz, C_6D_6 , 295 K) δ [ppm] = -114.74 (s, 1F, C_{ArF}); **IR** (ATR) $\tilde{\nu}$ [cm^{-1}] = 3249 (w), 2973 (w), 2931 (w), 2834 (w), 2038 (w), 1888 (w), 1736 (w), 1605 (m), 1573 (w), 1534 (s), 1517 (s), 1441(m), 1406 (w), 1386 (w), 1346 (w), 1324 (m), 1287 (m), 1243 (s), 1174 (s), 1157 (m), 1094 (w), 1031 (m), 952 (w), 826 (s), 793 (s), 737 (m), 665 (m); **HR-MS** (MALDI): $\text{C}_{35}\text{H}_{33}\text{AuClFN}_2\text{O}_2$ $[\text{M}]^+$ calcd.: 764.1880, found: 764.1875, $\Delta m/z$ = 0.654 ppm; **UV/VIS** (CH_2Cl_2) λ_{max} (ϵ) [nm ($\text{l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$)] = 335(609044), 386 (538576), 422 (548643), 490 (1440), 620 (221), 667 (292), 742 (242); **Elemental Analysis** calcd. for $\text{C}_{35}\text{H}_{33}\text{AuClFN}_2\text{O}_2$: C: 54.95, H: 4.35, N : 3.66, found C: 54.90, H: 4.33, N: 3.67.

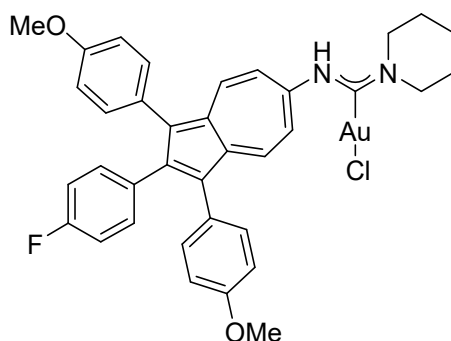
Synthesis of (((2-(4-fluorophenyl)-1,3-bis(4-methoxyphenyl)azulen-6-yl)amino)(pyrrolidin-1-yl)methylene)gold(I) chloride (14bb)



According to **GP1** 2-(4-fluorophenyl)-6-isocyano-1,3-bis(4-methoxyphenyl)azulene gold(I)chloride (**12b**) (50.0 mg, 72.3 μ mol, 1.00 eq.) and pyrrolidine (**13b**) (5.40 mg, 75.9 μ mol, 1.05 eq.) was stirred in dichloromethane at room temperature 12 hours. Purification by flash column chromatography (Silica, dichloromethane) yielded the title compound as a green solid (50.0 mg, 65.5 μ mol, 91%).

MP = 186 – 191 °C; **$^1\text{H}\{^{19}\text{F}\}$ NMR** (400 MHz, CD_2Cl_2 , 295 K) δ [ppm] = 8.18 (d, J = 10.8 Hz, 2H, $2\times\text{C}_{\text{ArH}}$), 7.56 (s, 1H, NH), 7.26 (d, J = 10.8 Hz, 2H, $2\times\text{C}_{\text{ArH}}$), 7.17 (d, J = 8.8 Hz, 4H, $4\times\text{C}_{\text{ArH}}$), 7.03 (dd, J = 8.9, 5.6 Hz, 2H, $2\times\text{C}_{\text{ArH}}$), 6.92 (d, J = 8.9 Hz, 4H, $4\times\text{C}_{\text{ArH}}$), 6.85 (t, J = 8.9 Hz, 2H, $-\text{CH}_2-$), 4.07 (t, J = 6.9 Hz, 2H, $-\text{CH}_2-$), 3.83 (s, 6H, $2\times\text{-OCH}_3$), 3.41 (t, J = 7.1 Hz, 2H, $-\text{CH}_2-$), 2.23 – 2.11 (m, 2H, $-\text{CH}_2-$), 1.97 (p, J = 7.0 Hz, 2H, $-\text{CH}_2-$); **$^{13}\text{C}\{^{19}\text{F}, ^1\text{H}\}$ NMR** (101 MHz, CD_2Cl_2 , 295 K) δ [ppm] = 189.04 (s, 1C, $\text{C}_{\text{Carbene}}$), 159.05 (s, 2C, $2\times\text{C}_{\text{Ar}}$), 148.05 (s, 2C, $2\times\text{C}_{\text{Ar}}$), 147.07 (s, 2C, $2\times\text{C}_{\text{Ar}}$), 136.01 (s, 2C, $2\times\text{C}_{\text{Ar}}$), 134.67 (d, 1C, C_{ArH}), 133.32 (d, 1C, C_{ArH}), 133.24 (d, 2C, $2\times\text{C}_{\text{ArH}}$), 132.85 (d, 2C, $2\times\text{C}_{\text{ArH}}$), 131.03 (s, 2C, $2\times\text{C}_{\text{Ar}}$), 128.31 (s, 2C, $2\times\text{C}_{\text{Ar}}$), 119.61 (d, 2C, $2\times\text{C}_{\text{ArH}}$), 115.12 (d, 2C, $2\times\text{C}_{\text{ArH}}$), 114.91 (d, 2C, $2\times\text{C}_{\text{ArH}}$), 114.13 (d, 2C, $2\times\text{C}_{\text{ArH}}$), 57.52 (t, 1C, $-\text{CH}_2-$), 55.65 (q, 2C, $2\times\text{-OCH}_3$), 46.81 (t, 1C, $-\text{CH}_2-$), 25.83 (t, 1C, $-\text{CH}_2-$), 24.67 (t, 1C, $-\text{CH}_2-$); **$^{19}\text{F}\{^1\text{H}\}$ NMR** (283 MHz, CD_2Cl_2 , 298 K) δ [ppm] = -116.21 (s, 1F, C_{ArF}); **IR** (ATR) $\tilde{\nu}$ [cm^{-1}] = 3352 (w), 2969 (w), 2929 (w), 2871 (w), 2834 (w), 1604 (m), 1573 (w), 1541 (s), 1515 (s), 1442 (m), 1405 (w), 1387 (w), 1351 (m), 1310 (m), 1287 (m), 1238 (s), 1175 (s), 1158 (m), 1109 (w), 1025 (m), 915 (w), 828 (m), 792 (s), 663 (w), 629 (w); **UV/VIS** (CH_2Cl_2) λ_{max} (ϵ) [nm ($\text{l}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$)] = 336 (65237), 390 (9576), 420 (5862), 620 (332), 660 (298), 746 (97); **HR-MS** (MALDI): $\text{C}_{35}\text{H}_{31}\text{Au}^{35}\text{ClFN}_2\text{O}_2$ $[\text{M}]^+$ calcd.: 762.1724, found.: 762.1713, $\text{C}_{35}\text{H}_{31}\text{Au}^{37}\text{ClFN}_2\text{O}_2$ $[\text{M}]^+$ calcd.: 764.1697, found.: 764.1698, $\Delta\text{m/z}$ = 0.131 ppm; **Elemental Analysis** calcd. for $\text{C}_{35}\text{H}_{31}\text{AuClFN}_2\text{O}_2$: C: 55.09, H: 4.10, N : 3.67, found C: 54.65, H: 4.45, N: 3.43.

Synthesis of (((2-(4-fluorophenyl)-1,3-bis(4-methoxyphenyl)azulen-6-yl)amino)(piperidin-1-yl)methylene)gold(I) chloride (14bc)

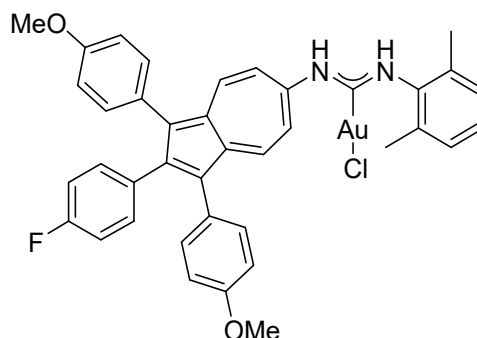


According to **GP1** 2-(4-fluorophenyl)-6-isocyano-1,3-bis(4-methoxyphenyl)azulene gold(I)chloride (**12b**) (50.0 mg, 72.3 μ mol, 1.00 eq.) and piperidine (**13c**) (6.46 mg, 75.9 μ mol, 1.05 eq.) was stirred in dichloromethane at room temperature 12 hours. Purification by flash column chromatography (Silica, dichloromethane) yielded the title compound as a green solid (49.0 mg, 63.1 μ mol, 87%).

According to **GP2** [AuCl(DMS)] (**11**) (52.6 mg, 178.6 μ mol, 1.00 eq.) and 2-(4-fluorophenyl)-6-isocyano-1,3-bis(4-methoxyphenyl)azulene (**10b**) (82.0 mg, 178 μ mol, 1.00 eq.) were stirred in dichloromethane for 1 hour at room temperature. Afterwards, piperidine (**13c**) (16.0 mg, 187 μ mol, 1.05 eq.) was added, the mixture stirred at room temperature for additional 12 hours. Purification by flash column chromatography (Silica, dichloromethane) yielded the title compound as a green solid (115 mg, 148 μ mol, 83%).

MP = 174 – 179 °C; **$^1\text{H}\{^{19}\text{F}\}$ NMR** (500 MHz, THF- d_8 , 295 K) δ [ppm] = 9.23 (s, 1H, NH), 8.05 (d, J = 10.9 Hz, 2H, $2x\text{C}_{\text{ArH}}$), 7.24 – 7.13 (m, 2H, $2x\text{C}_{\text{ArH}}$), 7.04 (d, J = 8.7 Hz, 4H, $4x\text{C}_{\text{ArH}}$), 6.91 (dd, J = 8.9, 5.6 Hz, 2H, $2x\text{C}_{\text{ArH}}$), 6.80 (d, J = 8.8 Hz, 4H, $4x\text{C}_{\text{ArH}}$), 6.74 (t, J = 8.9 Hz, 2H, $2x\text{C}_{\text{ArH}}$), 4.04 – 4.01 (m, 2H, $-\text{CH}_2-$), 3.68 (s, 6H, $2x\text{-OCH}_3$), 3.53 – 3.48 (m, 2H, $-\text{CH}_2-$), 1.52 (p, J = 2.9 Hz, 4H, $2x\text{-CH}_2-$), 1.46 (q, J = 5.9 Hz, 2H, $-\text{CH}_2-$); **$^{13}\text{C}\{^{19}\text{F}, ^1\text{H}\}$ NMR** (126 MHz, THF- d_8 , 295 K) δ [ppm] = 190.47 (s, 1C, $\text{C}_{\text{Carbene}}$), 162.66 (s, 1C, C_{Ar}), 160.71 (s, 1C, C_{Ar}), 158.65 (s, 2C, $2x\text{C}_{\text{Ar}}$), 149.56 (s, 1C, C_{Ar}), 145.51 (s, 1C, C_{Ar}), 135.55 (s, 1C, C_{Ar}), 133.96 (d, 2C, $2x\text{C}_{\text{ArH}}$), 133.13 (s, 2C, $2x\text{C}_{\text{Ar}}$), 133.10 (s, 1C, C_{Ar}), 132.85 (d, 1C, C_{ArH}), 132.79 (d, 1C, C_{ArH}), 132.26 (d, 2C, $2x\text{C}_{\text{ArH}}$), 132.21 (d, 1C, C_{ArH}), 129.72 (s, 1C, C_{Ar}), 128.07 (d, 1C, C_{ArH}), 128.01 (s, 1C, C_{Ar}), 120.01 (d, 2C, $2x\text{C}_{\text{ArH}}$), 114.50 (d, 2C, $2x\text{C}_{\text{ArH}}$), 114.33 (d, 2C, $2x\text{C}_{\text{ArH}}$), 113.56 (d, 2C, $2x\text{C}_{\text{ArH}}$), 58.55 (t, 1C, $-\text{CH}_2-$), 54.38 (q, 2C, $-\text{OCH}_3$), 46.53 (t, 1C, $-\text{CH}_2-$), 26.51 (t, 1C, $-\text{CH}_2-$), 25.75 (t, 1C, $-\text{CH}_2-$), 24.84 (t, 1C, $-\text{CH}_2-$); **$^{19}\text{F}\{^1\text{H}\}$ NMR** (471 MHz, THF- d_8 , 295 K) δ [ppm] = -116.85 (s, 1F, C_{ArF}); **IR** (ATR) $\tilde{\nu}$ [cm^{-1}] = 3261 (w), 3059 (w), 3021 (w), 2943 (w), 2856 (w), 2836 (w), 1605 (m), 1574 (m), 1551(m), 1538 (s), 1516 (s), 1473 (s), 1441 (m), 1405 (m), 1386 (m), 1350 (m), 1318 (w), 1286 (m), 1245(m), 1219 (s), 1175 (s), 1156(s), 1108 (m), 1089 (w), 1021 (s), 945 (w), 877 (w), 852 (m), 833 (m), 816 (m), 793 (s), 731 (s), 702 (w), 666 (m), 644 (m); **HR-MS** (MALDI): $\text{C}_{36}\text{H}_{33}\text{AuClFN}_2\text{O}_2$ [M] $^+$ calcd.:776.1880, found.:776.1884, $\Delta m/z$ = 0.515 ppm; **UV/VIS** (CH_2Cl_2) λ_{max} (ϵ) [nm ($\text{l}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$)] = 257 (1817), 338 (5028), 382 (788), 416 (468), 618 (251), 666 (224), 750 (82); **Elemental Analysis** calcd. for $\text{C}_{36}\text{H}_{33}\text{AuClFN}_2\text{O}_2$: C: 55.64, H: 4.28, N : 3.61, found C: 55.20, H: 4.72, N: 3.22.

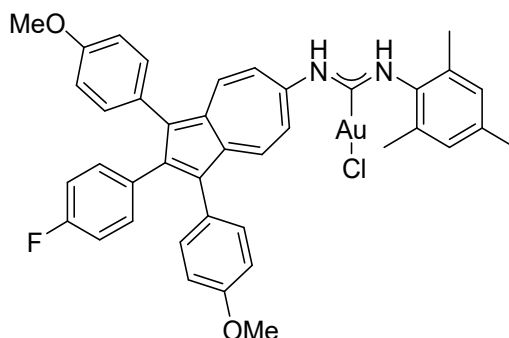
Synthesis of (((2,6-dimethylphenyl)amino)((2-(4-fluorophenyl)-1,3-bis(4-methoxyphenyl)azulen-6-yl)amino)methylene)gold(I) chloride (14bd)



According to **GP1** 2-(4-fluorophenyl)-6-isocyano-1,3-bis(4-methoxyphenyl)azulene gold(I)chloride (**12b**) (50.0 mg, 72.3 μmol , 1.00 eq.) and 2,6-dimethylaniline (**13d**) (9.19 mg, 75.9 μmol , 1.05 eq.) was stirred in dichloromethane at room temperature 12 hours. Purification by flash column chromatography (Silica, dichloromethane) yielded the title compound as a blue solid (42.0 mg, 51.7 μmol , 71%).

MP = 220 – 225 $^{\circ}\text{C}$; **$^1\text{H}\{^{19}\text{F}\}$ NMR** (600 MHz, CD_2Cl_2 , 295 K) δ [ppm] = 8.19 (d, J = 11.0 Hz, 2H, 2x C_{ArH}), 7.94 (s, 1H, C_{ArH}), 7.20 (s, 1H, C_{ArH}), 7.18 (d, J = 8.5 Hz, 6H, 6x C_{ArH}), 7.02 (dd, J = 8.8, 5.8 Hz, 2H, 2x C_{ArH}), 6.91 (d, J = 8.8 Hz, 5H, 5x C_{ArH}), 6.88 – 6.84 (m, 2H, 2x C_{ArH}), 3.83 (s, 6H, 2x- OCH_3), 1.56 (s, 3H, - CH_3), 1.55 (s, 3H, - CH_3); **$^{13}\text{C}\{^{19}\text{F}, ^1\text{H}\}$ NMR** (151 MHz, CD_2Cl_2 , 295 K) δ [ppm] = 191.59 (s, 1C, $\text{C}_{\text{Carbene}}$), 162.97 (s, 1C, C_{Ar}), 161.34 (s, 2C, 2x C_{Ar}), 158.95 (s, 4C, 4x C_{Ar}), 148.28 (s, 2C, 2x C_{Ar}), 147.23 (s, 2C, 2x C_{Ar}), 136.10 (s, 2C, 2x C_{Ar}), 134.49 (d, 2C, 2x C_{ArH}), 133.26 (d, 2C, 2x C_{ArH}), 133.21 (d, 1C, C_{ArH}), 132.81 (d, 4C, 4x C_{ArH}), 130.93 (s, 1C, C_{Ar}), 128.18 (s, 1C, C_{Ar}), 120.43 (d, 2C, 2x C_{ArH}), 115.06 (d, 2C, 2x C_{ArH}), 114.92 (d, 2C, 2x C_{ArH}), 114.05 (d, 4C, 4x C_{ArH}), 55.59 (q, 2C, 2x- OCH_3), 21.05 (q, 2C, 2x- CH_3); **$^{19}\text{F}\{^1\text{H}\}$ NMR** (283 MHz, CD_2Cl_2 , 295 K) δ [ppm] = -116.18 (s, 1F, C_{ArF}); **IR** (ATR) $\tilde{\nu}$ [cm^{-1}] = 3302 (w), 3188 (w), 2955 (w), 2928 (w), 2834 (w), 1606 (m), 1536 (s), 1517 (s), 1496 (s), 1470 (m), 1441 (m), 1389 (m), 1347 (m), 1287 (w), 1242 (m), 1195 (s), 1173 (w), 1155 (m), 1106 (w), 1090 (w), 1031 (m), 952 (w), 818 (m), 792 (m), 772 (m), 736 (m), 654 (w); **HR-MS** (MALDI): $\text{C}_{39}\text{H}_{33}\text{AuClFN}_2\text{O}_2$ [$\text{M}+\text{H}$] $^{+}$ calcd.: 812.1882, found: 812.1880, $\Delta m/z$ = 0.246 ppm; **UV/VIS** (CH_2Cl_2) λ_{max} (ϵ) [nm ($\text{l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$)] = 270 (28233), 333 (65501), 388 (9486), 425 (4517), 625 (325), 677 (271); **Elemental Analysis** calcd. for $\text{C}_{39}\text{H}_{33}\text{AuClFN}_2\text{O}_2$: C: 57.61, H: 4.09, N : 3.45, found C: 56.37, H: 4.20, N: 3.34.

Synthesis of (((2-(4-fluorophenyl)-1,3-bis(4-methoxyphenyl)azulen-6-yl)amino)(mesitylamino)methylene)gold(I) chloride (14be)



According to **GP1** 2-(4-fluorophenyl)-6-isocyano-1,3-bis(4-methoxyphenyl)azulene gold(I)chloride (**12d**) (50.0 mg, 72.3 μmol , 1.00 eq.) and mesitylamine (**13e**) (10.2 mg, 75.9 μmol , 1.05 eq.) was stirred in dichloromethane at room temperature 12 hours. Purification by flash column chromatography (Silica, dichloromethane) yielded the title compound as a blue solid (44.0 mg, 53.2 μmol , 74%).

MP = 204 – 209 °C; **$^1\text{H}\{^{19}\text{F}\}$ NMR** (500 MHz, CD_2Cl_2 , 295 K) δ 8.86 (s, 1H, NH), 8.15 (d, J = 10.9 Hz, 2H, $2\times\text{C}_{\text{ArH}}$), 7.89 (s, 1H, NH), 7.17 – 7.13 (m, 6H, $6\times\text{C}_{\text{ArH}}$), 7.03 – 7.00 (m, 4H, $4\times\text{C}_{\text{ArH}}$), 6.91 (d, J = 8.7 Hz, 4H, $4\times\text{C}_{\text{ArH}}$), 6.85 (d, J = 8.8 Hz, 2H, $2\times\text{C}_{\text{ArH}}$), 3.83 (s, 3H, -OCH₃), 2.32 (s, 3H, -CH₃), 2.26 (s, 6H, $2\times\text{-CH}_3$); **$^{13}\text{C}\{^{19}\text{F}, ^1\text{H}\}$ NMR** (126 MHz, CD_2Cl_2 , 295 K) δ [ppm] = 190.16 (s, 1C, $\text{C}_{\text{Carbene}}$), 162.18 (s, 2C, $2\times\text{C}_{\text{Ar}}$), 158.98 (s, 2C, $2\times\text{C}_{\text{Ar}}$), 147.37 (s, 2C, $2\times\text{C}_{\text{Ar}}$), 147.11 (s, 2C, $2\times\text{C}_{\text{Ar}}$), 140.36 (s, 2C, $2\times\text{C}_{\text{Ar}}$), 136.14 (s, 2C, $2\times\text{C}_{\text{Ar}}$), 135.85 (s, 2C, $2\times\text{C}_{\text{Ar}}$), 134.48 (d, 2C, $2\times\text{C}_{\text{ArH}}$), 133.23 (s, 1C, C_{Ar}), 132.98 (d, 2C, $2\times\text{C}_{\text{Ar}}$), 132.79 (d, 2C, $2\times\text{C}_{\text{ArH}}$), 131.08 (s, 1C, C_{Ar}), 130.48 (d, 2C, $2\times\text{C}_{\text{ArH}}$), 129.69 (d, 2C, $2\times\text{C}_{\text{ArH}}$), 128.08 (d, 2C, $2\times\text{C}_{\text{ArH}}$), 119.57 (d, 2C, $2\times\text{C}_{\text{ArH}}$), 115.01 (d, 2C, $2\times\text{C}_{\text{ArH}}$), 114.06 (d, 2C, $2\times\text{C}_{\text{ArH}}$), 55.59 (q, 2C, $2\times\text{-OCH}_3$), 21.19 (q, 1C, -CH₃), 18.52 (q, 2C, $2\times\text{-CH}_3$); **$^{19}\text{F}\{^1\text{H}\}$ NMR** (283 MHz, CD_2Cl_2 , 298 K) δ [ppm] = -116.01 (s, 1F, -C_{Ar}F); **IR** (ATR) $\tilde{\nu}$ [cm^{-1}] = 3201 (w), 2932 (w), 2833 (w), 1606 (m), 1516 (s), 1441 (m), 1388 (m), 1286 (m), 1242 (s), 1173 (s), 1156 (m), 1106 (w), 1031 (m), 833 (m), 792 (m); **UV/VIS** (CH_2Cl_2) λ_{max} (ϵ) [nm ($\text{l}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$)] = 334 (61439), 390 (9378), 414 (5659), 624 (329), 672 (291), 767 (81); **HR-MS** (MALDI): $\text{C}_{40}\text{H}_{35}\text{Au}^{35}\text{ClFN}_2\text{O}_2$ $[\text{M}]^+$ calcd.: 826.2037, found.: 826.2017, $\Delta m/z$ = 2.421 ppm, $\text{C}_{40}\text{H}_{35}\text{Au}^{37}\text{ClFN}_2\text{O}_2$ $[\text{M}]^+$ calcd.: 828.2007, found.: 828.2010, $\Delta m/z$ = 0.362 ppm; **Elemental Analysis** calcd. for $\text{C}_{40}\text{H}_{35}\text{AuClFN}_2\text{O}_2$: C: 58.08, H: 4.27, N : 3.39, found C: 58.69, H: 4.45, N: 3.51.

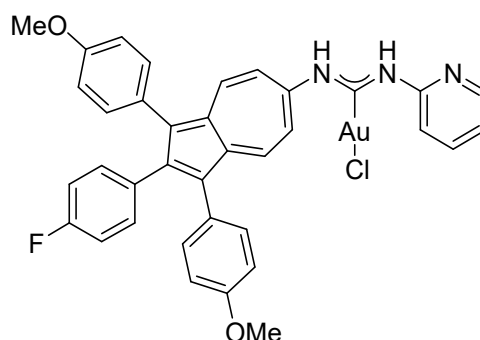
Chemical structure of compound 10: A fluorene derivative with a 4-methoxyphenyl group at position 2, a 4-fluorophenyl group at position 3, and a 4-methoxyphenyl group at position 9. The fluorene core is substituted at position 1 with a 1,2-bis(isopropyl)hydrazine-5-ylidene group.

According to **GP2** [AuCl(DMS)] (**11**) (52.6 mg, 178.6 μ mol, 1.00 eq.) and 2-(4-fluorophenyl)-6-isocyano-1,3-bis(4-methoxyphenyl)azulene (**10b**) (82.0 mg, 178 μ mol, 1.00 eq.) were stirred in dichloromethane for 1 hour at room temperature. Afterwards, 2,6-diisopropylaniline (**13f**) (47.5 mg, 179 μ mol, 1.50 eq.) was added, the mixture stirred at room temperature for additional 12 hours. Purification by flash column chromatography (Silica, dichloromethane) yielded the title compound as a green solid (86.0 mg, 111 μ mol, 62%).

S37

(ATR) $\tilde{\nu}$ [cm⁻¹] = 3203, 2963, 2933, 2871, 2836, 1662, 1606, 1573, 1518, 1463, 1443, 1386, 1287, 1243, 1175, 1156, 1106, 1059, 1032, 952, 936, 827, 793, 754, 662; **HR-MS** (MALDI): C₄₃H₄₁AuClFN₂O₂ [M]⁺ calcd.: 868.2506, found.: 868.2519, $\Delta m/z$ = 1.497 ppm; **UV/VIS** (CH₂Cl₂) $\lambda_{\max}$ (ϵ) [nm (l*mol⁻¹*cm⁻¹)] = 264 (17068), 333 (37476), 383 (6679), 417 (3636), 494 (249), 625 (217), 678 (186); **Elemental Analysis** calcd. for C₄₃H₄₁AuClFN₂O₂: C: 59.42, H: 4.75, N : 3.22, found C: 59.27, H: 5.29, N: 3.14.

Synthesis of (((2-(4-fluorophenyl)-1,3-bis(4-methoxyphenyl)azulen-6-yl)amino)(pyridin-2-ylamino)methylene)gold(I) chloride (14bg)

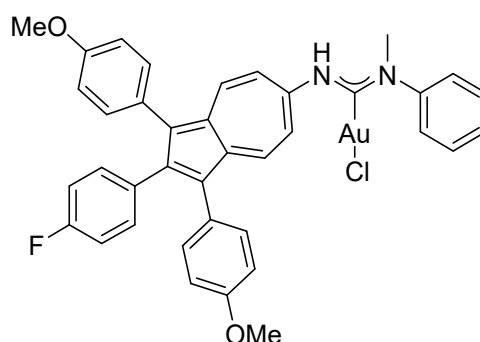


According to **GP1** 2-(4-fluorophenyl)-6-isocyano-1,3-bis(4-methoxyphenyl)azulene gold(I)chloride (**12b**) (50.0 mg, 72.3 μ mol, 1.00 eq.) and pyridine-2-amine (**13g**) (7.14 mg, 75.9 μ mol, 1.05 eq.) was stirred in dichloromethane at room temperature 12 hours. Purification by flash column chromatography (Silica, dichloromethane) yielded the title compound as a blue solid (44.0 mg, 56.0 μ mol, 77%).

MP = 252 – 257 °C; **¹H{¹⁹F} NMR** (500 MHz, CD₂Cl₂, 295 K) δ [ppm] = 14.79 (s, 1H, NH), 10.25 (s, 1H, NH), 8.28 (d, J = 3.2 Hz, 1H, C_{Ar}H), 8.18 (d, J = 10.8 Hz, 2H, 2xC_{Ar}H), 7.71 – 7.64 (m, 1H, C_{Ar}H), 7.38 (d, J = 11.0 Hz, 2H, 2xC_{Ar}H), 7.27 (d, J = 8.2 Hz, 1H, C_{Ar}H), 7.14 (d, J = 8.7 Hz, 5H, 5xC_{Ar}H), 7.03 – 6.98 (m, 2H, 2xC_{Ar}H), 6.90 (d, J = 8.8 Hz, 4H, 4xC_{Ar}H), 6.86 (t, J = 8.9 Hz, 2H, 2xC_{Ar}H), 3.82 (s, 6H, 2x-OCH₃); **¹³C{¹⁹F, ¹H} NMR** (126 MHz, CD₂Cl₂, 295 K) δ [ppm] = 189.82 (s, 1C, C_{Carbene}), 163.15 (s, 1C, C_{Ar}), 161.19 (s, 1C, C_{Ar}), 158.94 (s, 2C, 2xC_{Ar}), 154.82 (s, 2C, 2xC_{Ar}), 148.12 (s, 1C, C_{Ar}), 147.22 (s, 2C, 2xC_{Ar}), 146.09 (d, 1C, C_{Ar}H), 139.69 (d, 1C, C_{Ar}H), 136.13 (s, 2C, 2xC_{Ar}), 134.68 (d, 2C, 2xC_{Ar}H), 133.28 (d, 1C, C_{Ar}H), 133.22 (d, 4C, 4xC_{Ar}H), 132.80 (d, 1C, C_{Ar}H), 130.81 (s, 1C, C_{Ar}), 128.14 (s, 1C, C_{Ar}), 120.75 (d, 1C, C_{Ar}H), 119.59 (d, 2C, 2xC_{Ar}H), 115.10 (d, 1C, C_{Ar}H), 114.93 (d, 1C, C_{Ar}H), 114.77 (d, 1C, C_{Ar}H), 114.07 (d, 4C, 4xC_{Ar}H), 55.59 (q, 2C, 2x-OCH₃); **¹⁹F{¹H} NMR** (283 MHz, CD₂Cl₂, 295 K) δ [ppm] = -116.06 (s, 1F, -C_{Ar}F); **IR** (ATR) $\tilde{\nu}$ [cm⁻¹] = 3249 (w), 3188 (w), 3116 (w), 3053 (w), 2931 (w), 2833 (w), 1734 (w), 1605 (m), 1515 (s), 1476 (m), 1430 (s),

1371 (m), 1320 (w), 1286 (m), 1242 (s), 1173 (s), 1154 (m), 1106 (w), 1030 (m), 826 (s), 776 (s), 734 (m), 633 (w); **UV/VIS** (CH₂Cl₂) λ_{max} (ϵ) [nm (l*mol⁻¹*cm⁻¹)] = 285 (34968), 342 (64717), 422 (8037), 626 (355), 667 (319), 757 (102); **HR-MS** (MALDI): C₃₆H₂₈Au³⁵ClFN₃O₂ [M]⁺ calcd.: 785.1520, found.: 785.1502, $\Delta m/z$ = 2.292 ppm, C₃₆H₂₈Au³⁷ClFN₃O₂ [M]⁺ calcd.: 787.1490, found.: 787.1488, $\Delta m/z$ = 0.254 ppm; **Elemental Analysis** calcd. for C₃₆H₂₈AuClFN₂O₂: C: 55.63, H: 4.13, N: 5.27, found C: 55.59, H: 3.83, N: 5.31.

Synthesis of (((2-(4-fluorophenyl)-1,3-bis(4-methoxyphenyl)azulen-6-yl)amino)(methyl(phenyl)amino)methylene)gold(I) chloride (14bh)

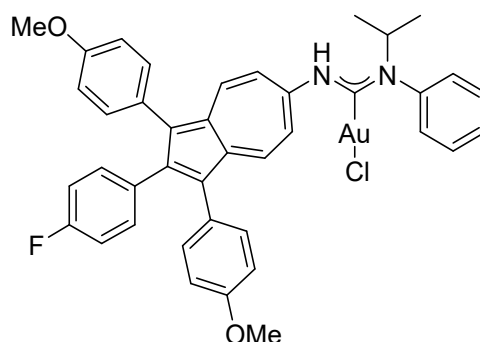


According to **GP1** 2-(4-fluorophenyl)-6-isocyano-1,3-bis(4-methoxyphenyl)azulene gold(I)chloride (**12b**) (50.0 mg, 72.3 μ mol, 1.00 eq.) and *N*-methylaniline (**13h**) (8.13 mg, 75.9 μ mol, 1.05 eq.) was stirred in dichloromethane at room temperature 12 hours. Purification by flash column chromatography (Silica, dichloromethane) yielded the title compound as a blue solid (51.0 mg, 63.8 μ mol, 88%).

MP = 210 – 215 °C; **¹H{¹⁹F} NMR** (300 MHz, CD₂Cl₂, 295 K) δ [ppm] = 8.04 (d, J = 10.8 Hz, 2H, 2xC_{Ar}H), 7.54 – 7.46 (m, 3H, 3xC_{Ar}H), 7.46 – 7.38 (m, 1H, C_{Ar}H), 7.30 (s, 1H, NH), 7.20 (dd, J = 8.3, 1.4 Hz, 2H, 2xC_{Ar}H), 7.05 (d, J = 8.8 Hz, 4H, 4xC_{Ar}H), 6.99 (s, 1H, C_{Ar}H), 6.95 – 6.89 (m, 2H, 2xC_{Ar}H), 6.80 (d, J = 8.9 Hz, 4H, 4xC_{Ar}H), 6.78 – 6.71 (m, 2H, 2xC_{Ar}H), 3.78 (s, 3H, -CH₃), 3.72 (s, 6H, 2x-OCH₃); **¹³C{¹⁹F, ¹H} NMR** (75 MHz, CD₂Cl₂, 295 K) δ [ppm] = 193.11 (s, 1C, C_{Carbene}), 163.82 (s, 1C, C_{Ar}), 160.56 (s, 1C, C_{Ar}), 159.00 (s, 2C, 2x C_{Ar}), 148.91 (s, 1C, C_{Ar}), 147.40 (s, 2C, 2xC_{Ar}), 140.52 (s, 2C, 2xC_{Ar}), 136.15 (s, 2C, 2xC_{Ar}), 134.43 (d, 1C, C_{Ar}H), 133.29 (d, 1C, C_{Ar}H), 133.18 (d, 4C, 4xC_{Ar}H), 132.80 (d, 1C, C_{Ar}H), 131.79 (d, 2C, 2xC_{Ar}H), 131.00 (s, 1C, C_{Ar}), 130.43 (d, 1C, C_{Ar}H), 129.94 (d, 1C, C_{Ar}H), 128.13 (s, 1C, C_{Ar}), 126.72 (d, 2C, 2xC_{Ar}H), 120.14 (d, 2C, 2xC_{Ar}H), 115.15 (d, 1C, C_{Ar}H), 114.86 (d, 1C, C_{Ar}H), 114.09 (d, 4C, 4xC_{Ar}H), 55.60 (q, 2C, 2x-OCH₃), 49.56 (q, 1C, -CH₃); **¹⁹F{¹H} NMR** (283 MHz, CD₂Cl₂, 298 K) δ [ppm] = -116.03 (s, 1F, -C_{Ar}F); **IR** (ATR) $\tilde{\nu}$ [cm⁻¹] = 3325 (w), 2834 (w), 1732 (w), 1605 (m), 1515 (s), 1492 (m), 1441 (m), 1387 (m), 1342 (m), 1286 (m), 1242

(s), 1174 (s), 1157 (m), 1106 (w), 1030 (s), 831 (s), 793 (m), 768 (m), 698 (m); **UV/VIS** (CH_2Cl_2) λ_{max} (ϵ) [nm ($\text{l}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$)] = 335 (109661), 388 (10282), 423 (20243), 621 (314), 667 (192), 765 (21); **HR-MS** (MALDI): $\text{C}_{38}\text{H}_{31}\text{Au}^{35}\text{ClFN}_2\text{O}_2$ $[\text{M}]^+$ calcd.: 798.1724 found.: 798.1712, $\Delta m/z = 1.503$ ppm, $\text{C}_{38}\text{H}_{31}\text{Au}^{37}\text{ClFN}_2\text{O}_2$ $[\text{M}]^+$ calcd.: 800.1694, found.: 800.1700, $\Delta m/z = 0.750$ ppm; **Elemental Analysis** calcd. for $\text{C}_{38}\text{H}_{31}\text{AuClFN}_2\text{O}_2$: C: 57.12, H: 3.91, N: 3.51, found C: 56.77, H: 4.17, N: 3.47.

Synthesis of (((2-(4-fluorophenyl)-1,3-bis(4-methoxyphenyl)azulen-6-yl)amino)(isopropyl(phenyl)amino)methylene)gold(I) chloride (14bi)

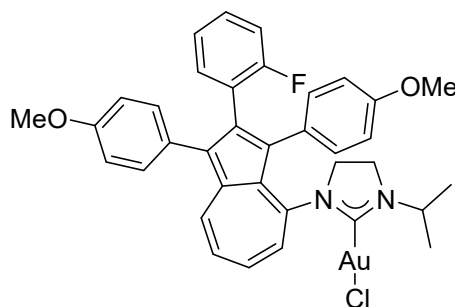


According to **GP1** 2-(4-fluorophenyl)-6-isocyano-1,3-bis(4-methoxyphenyl)azulene gold(I)chloride (**12b**) (50.0 mg, 72.3 μmol , 1.00 eq.) and *N*-isopropylaniline (**13i**) (10.3 mg, 75.9 μmol , 1.05 eq.) was stirred in dichloromethane at room temperature 12 hours. Purification by flash column chromatography (Silica, dichloromethane) yielded the title compound as a blue solid (48.0 mg, 58.0 μmol , 80%).

MP = 196 – 201 $^{\circ}\text{C}$; **$^1\text{H}\{^{19}\text{F}\}$ NMR** (500 MHz, CD_2Cl_2 , 295 K) δ [ppm] = 8.04 (d, $J = 11.0$ Hz, 2H, $2x\text{C}_{\text{ArH}}$), 7.56 – 7.49 (m, 2H, $2x\text{C}_{\text{ArH}}$), 7.48 – 7.43 (m, 1H, C_{ArH}), 7.32 (s, 1H, NH), 7.13 (dd, $J = 8.4, 1.3$ Hz, 2H, $2x\text{C}_{\text{ArH}}$), 7.05 (d, $J = 8.7$ Hz, 4H, $4x\text{C}_{\text{ArH}}$), 7.00 (d, $J = 11.1$ Hz, 2H, $2x\text{C}_{\text{ArH}}$), 6.91 (dd, $J = 8.9, 5.6$ Hz, 2H, $2x\text{C}_{\text{ArH}}$), 6.80 (d, $J = 8.8$ Hz, 4H, $4x\text{C}_{\text{ArH}}$), 6.74 (t, $J = 8.9$ Hz, 2H, $2x\text{C}_{\text{ArH}}$), 5.44 (p, $J = 6.8$ Hz, 1H, $-\text{CH}(\text{CH}_3)_2$), 3.72 (s, 6H, $-\text{OCH}_3$), 1.13 (d, $J = 6.8$ Hz, 6H, $-\text{CH}(\text{CH}_3)_2$); **$^{13}\text{C}\{^{19}\text{F}, ^1\text{H}\}$ NMR** (126 MHz, CD_2Cl_2 , 295 K) δ [ppm] = 192.70 (s, 1C, $\text{C}_{\text{Carbene}}$), 163.11 (s, 1C, C_{Ar}), 161.16 (s, 1C, C_{Ar}), 158.93 (s, 2C, $2x\text{C}_{\text{Ar}}$), 147.85 (s, 2C, $2x\text{C}_{\text{Ar}}$), 147.24 (s, 2C, $2x\text{C}_{\text{Ar}}$), 136.11 (s, 2C, $2x\text{C}_{\text{Ar}}$), 135.33 (s, 1C, C_{Ar}), 134.39 (d, 2C, $2x\text{C}_{\text{ArH}}$), 133.24 (d, 4C, $4x\text{C}_{\text{ArH}}$), 133.18 (d, 1C, C_{ArH}), 132.78 (d, 1C, C_{ArH}), 131.18 (d, 2C, $2x\text{C}_{\text{ArH}}$), 130.85 (s, 1C, C_{Ar}), 130.62 (d, 1C, C_{ArH}), 129.60 (d, 2C, $2x\text{C}_{\text{ArH}}$), 128.12 (s, 1C, C_{Ar}), 120.40 (d, 2C, $2x\text{C}_{\text{ArH}}$), 115.06 (d, 1C, C_{ArH}), 114.89 (d, 1C, C_{ArH}), 114.05 (d, 4C, $2x\text{C}_{\text{ArH}}$), 62.31 (d, 1C, $-\text{CH}(\text{CH}_3)_2$), 55.57 (q, 2C, $2x\text{-OCH}_3$), 21.90 (q, 2C, $2x\text{-CH}(\text{CH}_3)_2$); **$^{19}\text{F}\{^1\text{H}\}$ NMR** (283 MHz, CD_2Cl_2 , 298 K) δ [ppm] = -116.08 (s, 1F, $-\text{C}_{\text{ArF}}$); **IR** (ATR) $\tilde{\nu}$ [cm^{-1}]

^1J = 3333 (w), 2970 (w), 2834 (w), 1736 (w), 1604 (w), 1573 (w), 1530 (s), 1513 (s), 1489 (m), 1425 (w), 1357 (m), 1327 (m), 1285 (w), 1243 (s), 1174 (m), 1113 (m), 1028 (m), 851 (m), 792 (s), 702 (m), 662 (w); **UV/VIS** (CH_2Cl_2) λ_{max} (ϵ) [nm ($\text{l}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$)] = 282 (26919), 336 (64306), 385 (10468), 415 (5982), 622 (307), 663 (278), 756 (82); **HR-MS** (MALDI): $\text{C}_{40}\text{H}_{35}\text{Au}^{35}\text{ClFN}_2\text{O}_2$ $[\text{M}]^+$ calcd.: 826.2037, found.: 826.2023, $\Delta m/z$ = 1.694 ppm, $\text{C}_{40}\text{H}_{35}\text{Au}^{37}\text{ClFN}_2\text{O}_2$ $[\text{M}]^+$ calcd.: 828.2007, found.: 828.2012, $\Delta m/z$ = 0.604 ppm; **Elemental Analysis** calcd. for $\text{C}_{40}\text{H}_{35}\text{AuClFN}_2\text{O}_2$: C: 58.08, H: 4.92, N : 3.39, found C: 58.11, H: 4.66, N: 3.29.

Synthesis of (1-(2-(2-fluorophenyl)-1,3-bis(4-methoxyphenyl)azulen-4-yl)-3-isopropylimidazolidin-2-ylidene)gold(I) chloride (16a)

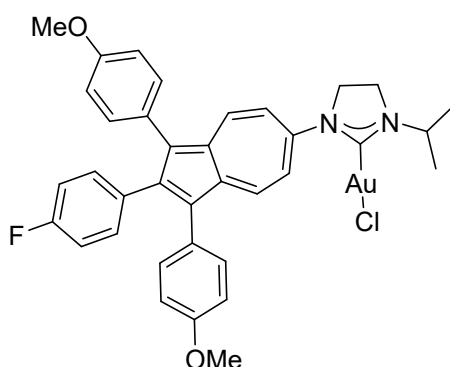


According to **GP1** 2-(2-fluorophenyl)-4-isocyano-1,3-bis(4-methoxyphenyl)azulene gold(I)chloride (**12a**) (50.0 mg, 72.3 μmol , 1.00 eq.) N-(2-chloroethyl)propan-2-amine hydrochloride (**15**) (11.99 mg, 75.9 μmol , 1.05 eq.) and triethylamine (**9**) (73.1 mg, 0.1 mL, 722 μmol , 10.0 eq.) was stirred in dichloromethane at room temperature 12 hours. Purification by flash column chromatography (Silica, dichloromethane) yielded the title compound as a blue solid (35.0 mg, 45.04 μmol , 60%).

MP = 225 – 230 $^{\circ}\text{C}$; $^1\text{H}\{^19\text{F}\}$ **NMR** (301 MHz, C_6D_6 , 295 K) δ [ppm] = 8.21 – 7.98 (m, 1H, C_{ArH}), 7.19 – 7.02 (m, 4H, C_{ArH}), 6.90 (d, J = 10.0 Hz, 1H, C_{ArH}), 6.77 – 6.62 (m, 2H, $2\times\text{C}_{\text{ArH}}$), 6.58 (s, 1H, C_{ArH}), 6.57 – 6.51 (m, 3H, $3\times\text{C}_{\text{ArH}}$), 6.46 (dd, J = 11.1, 4.3 Hz, 1H, C_{ArH}), 6.40 (dd, J = 8.5, 4.3 Hz, 1H, C_{ArH}), 6.29 (dd, J = 8.7, 2.9 Hz, 1H, C_{ArH}), 6.23 (dd, J = 8.3, 2.8 Hz, 1H, C_{ArH}), 4.40 (p, J = 6.7 Hz, 1H, $-\text{CH}(\text{CH}_3)_2$), 3.07 (s, 3H, $-\text{OCH}_3$), 2.98 (s, 3H, $-\text{OCH}_3$), 2.89 – 2.71 (m, 1H, $-\text{CH}_2-$), 2.29 (p, J = 11.1 Hz, 1H, $-\text{CH}_2-$), 2.00 – 1.87 (m, 1H, $-\text{CH}_2-$), 1.41 (q, J = 11.0 Hz, 1H, $-\text{CH}_2-$), 0.50 (d, J = 6.9 Hz, 3H, $-\text{CH}(\text{CH}_3)_2$), 0.45 (d, J = 6.7 Hz, 3H, $-\text{CH}(\text{CH}_3)_2$); $^{13}\text{C}\{^19\text{F}, ^1\text{H}\}$ **NMR** (101 MHz, C_6D_6 , 295 K) δ [ppm] = 194.14 (s, 1C, $\text{C}_{\text{Carbene}}$), 161.94 (s, 1C, C_{Ar}), 159.50 (s, 1C, C_{Ar}), 159.33 (s, 1C, C_{Ar}), 158.31 (s, 1C, C_{Ar}), 146.42 (s, 1C, C_{Ar}), 145.26 (s, 1C, C_{Ar}), 139.66 (s, 1C, C_{Ar}), 137.20 (d, 1C, C_{ArH}), 136.81 (d, 1C, C_{ArH}), 136.42 (d, 1C, C_{ArH}), 133.30 (d, 1C, C_{ArH}), 132.71 (s, 1C, C_{Ar}), 132.43 (d, 1C, C_{ArH}), 130.55

(d, 1C, $\underline{C_{Ar}H}$), 129.41 (s, 1C, $\underline{C_{Ar}}$), 129.28 (d, 1C, $\underline{C_{Ar}H}$), 129.09 (s, 1C, $\underline{C_{Ar}}$), 128.92 (s, 1C, $\underline{C_{Ar}}$), 125.83 (d, 1C, $\underline{C_{Ar}H}$), 125.71 (s, 1C, $\underline{C_{Ar}}$), 125.39 (d, 1C, $\underline{C_{Ar}H}$), 124.45 (d, 1C, $\underline{C_{Ar}H}$), 123.94 (d, 1C, $\underline{C_{Ar}H}$), 115.56 (d, 1C, $\underline{C_{Ar}H}$), 115.34 (d, 1C, $\underline{C_{Ar}H}$), 114.23 (d, 1C, $\underline{C_{Ar}H}$), 113.35 (d, 1C, $\underline{C_{Ar}H}$), 112.32 (d, 1C, $\underline{C_{Ar}H}$), 54.71 (q, 2C, 2x-OCH₃), 52.92 (t, 1C, -CH₂-), 52.00 (d, 1C, -CH(CH₃)₂), 42.15 (t, 1C, -CH₂-), 20.59 (q, 1C, -CH(CH₃)₂), 19.82 (q, 1C, -CH(CH₃)₂); **$^{19}\text{F}\{^1\text{H}\}$ NMR** (283 MHz, C₆D₆, 295 K) δ [ppm] = -112.99 (s, 1F, C_{Ar}F); **IR** (ATR) $\tilde{\nu}$ [cm⁻¹] = 2969 (w), 2931 (w), 2834 (w), 1738 (w), 1712 (w), 1608 (m), 1559 (m), 1504 (s), 1451 (s), 1356 (m), 1323 (m), 1269 (s), 1244 (s), 1204 (m), 1175 (m), 1107 (w), 1031 (m), 945 (w), 828 (m), 760 (m), 732 (w); **HR-MS** (MALDI): C₃₆H₃₃AuClFN₂O₂ [M]⁺ calcd.: 776.1880, found.: 776.1884, $\Delta m/z$ = 0.515 ppm; **UV/VIS** (CH₂Cl₂) λ_{max} (ϵ) [nm (l*mol⁻¹*cm⁻¹)] = 258 (29555), 293 (37450), 314 (35392), 619 (484), 665 (439), 733 (182); **Elemental Analysis** calcd. for C₃₆H₃₃AuClFN₂O: C: 55.64, H: 4.28, N: 3.61, found C: 55.78, H: 4.45, N: 3.70.

Synthesis of (1-(2-(4-fluorophenyl)-1,3-bis(4-methoxyphenyl)azulen-6-yl)-3-isopropylimidazolidin-2-ylidene)gold(I) chloride (16b)



According to **GP1** 2-(4-fluorophenyl)-6-isocyano-1,3-bis(4-methoxyphenyl)azulene gold(I)chloride (**12b**) (50.0 mg, 72.3 μmol , 1.00 eq.) N-(2-chloroethyl)propan-2-amine hydrochloride (**15**) (12.0 mg, 75.9 μmol , 1.05 eq.) and triethylamine (**9**) (73.1 mg, 0.1 mL, 722 μmol , 10.0 eq.) was stirred in dichloromethane at room temperature 12 hours. Purification by flash column chromatography (Silica, dichloromethane) yielded the title compound as a blue solid (48.0 mg, 61.8 μmol , 85%).

MP = 236 – 241 °C; **$^1\text{H}\{^{19}\text{F}\}$ NMR** (300 MHz, CD₂Cl₂, 295 K) δ [ppm] = 8.19 (d, J = 10.8 Hz, 2H, 2xC_{Ar}H), 7.26 (d, J = 10.8 Hz, 2H, 2xC_{Ar}H), 7.17 (d, J = 8.9 Hz, 4H, 4xC_{Ar}H), 7.03 (dd, J = 8.9, 5.6 Hz, 2H, 2xC_{Ar}H), 6.92 (d, J = 8.9 Hz, 4H, 4xC_{Ar}H), 6.85 (t, J = 8.9 Hz, 2H, 2xC_{Ar}H), 4.95 (hept, J = 6.6 Hz, 1H, -CH(CH₃)₂), 4.22 – 4.11 (m, 2H, -CH₂-), 3.83 (s, 6H, 2x-OCH₃), 3.80 – 3.70 (m, 2H, -CH₂-), 1.32 (d, J = 6.7 Hz, 6H, -CH(CH₃)₂); **$^{13}\text{C}\{^{19}\text{F}, ^1\text{H}\}$ NMR** (75 MHz, CD₂Cl₂, 295 K) δ [ppm] = 191.19 (s, 1C, $\underline{C_{Carbene}}$), 163.82 (s, 1C, $\underline{C_{Ar}}$), 160.57 (s, 2C, 2xC_{Ar}),

159.01 (s, 1C, $\underline{\text{C}}_{\text{Ar}}$), 149.26 (s, 2C, $2x\underline{\text{C}}_{\text{Ar}}$), 147.26 (s, 2C, $2x\underline{\text{C}}_{\text{Ar}}$), 136.19 (s, 2C, $2x\underline{\text{C}}_{\text{Ar}}$), 134.61 (d, 2C, $2x\underline{\text{C}}_{\text{ArH}}$), 133.32 (d, 4C, $4x\underline{\text{C}}_{\text{ArH}}$), 133.21 (d, 1C, $\underline{\text{C}}_{\text{ArH}}$), 132.82 (d, 4C, $4x\underline{\text{C}}_{\text{ArH}}$), 130.99 (s, 1C, $\underline{\text{C}}_{\text{Ar}}$), 128.24 (s, 1C, $\underline{\text{C}}_{\text{Ar}}$), 119.46 (d, 2C, $2x\underline{\text{C}}_{\text{ArH}}$), 115.14 (d, 2C, $2x\underline{\text{C}}_{\text{ArH}}$), 114.86 (d, 1C, $\underline{\text{C}}_{\text{ArH}}$), 114.10 (d, 4C, $2x\underline{\text{C}}_{\text{ArH}}$), 55.62 (q, 2C, $2x\text{-OCH}_3$); 51.79 (t, 1C, $-\underline{\text{CH}}_2-$), 43.72 (t, 1C, $-\underline{\text{CH}}_2-$), 20.69 (q, 2C, $-\text{CH}(\underline{\text{CH}}_3)_2$) [signal for $-\underline{\text{CH}}(\text{CH}_3)_2$ was not observed]; **$^{19}\text{F}\{^1\text{H}\}$ NMR** (283 MHz, CD_2Cl_2 , 298 K) δ [ppm] = -116.13 (s, 1F, $-\text{C}_{\text{ArF}}$); **IR** (ATR) $\tilde{\nu}$ [cm^{-1}] = 2966 (w), 2833 (w), 1605 (m), 1573 (m), 1545 (w), 1510 (s), 1470 (m), 1407 (s), 1349 (w), 1274 (s), 1242 (s), 1173 (s), 1156 (m), 1108 (w), 1031 (m), 949 (w), 828 (s), 792 (s), 662 (w); **UV/VIS** (CH_2Cl_2) λ_{max} (ϵ) [nm ($\text{l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$)] = 342 (66881), 418 (7236), 623 (295), 665 (277), 757 (80); **HR-MS** (MALDI): $\text{C}_{36}\text{H}_{33}\text{Au}^{35}\text{ClFN}_2\text{O}_2$ $[\text{M}]^+$ calcd.: 776.1880, found.: 776.1870, $\Delta m/z = 1.288$ ppm, $\text{C}_{36}\text{H}_{33}\text{Au}^{37}\text{ClFN}_2\text{O}_2$ $[\text{M}]^+$ calcd.: 778.1859, found.: 778.1856, $\Delta m/z = 0.386$ ppm; **Elemental Analysis** calcd. for $\text{C}_{36}\text{H}_{33}\text{AuClFN}_2\text{O}$: C: 55.64, H: 4.28, N: 3.61, found C: 55.86, H: 4.51, N: 3.70.

3 Cell viability assay

Cancerous (A2780, A2780*cis*, MDA-MB-231 and U87) cell lines were obtained from ATCC and cultured according to the supplier's recommendations. Cells were maintained in specify medium, supplemented with 10% fetal bovine serum (FBS, [supplier]), 1% penicillin-streptomycin, and incubated at 37 °C in a humidified atmosphere containing 5% CO_2 .

A total of 1.5×10^3 cells per well were seeded in 96-well white opaque plates (Corning, Costar®) and allowed to adhere overnight. Cells were treated with six concentrations (0.001, 0.01, 0.1, 1, 10, and 100 μM) of the gold carbene compounds. These concentrations were obtained by serial dilution in the respective culture medium from 10 mM stock solutions prepared in DMSO. The final DMSO concentration did not exceed 0.1% (v/v) in any well.

Cisplatin was used as a reference compound under identical experimental conditions. A 10 mM cisplatin stock solution was freshly prepared in sterile water before each experiment.

After 96 hours of treatment, cell viability was assessed using the CellTiter-Glo® Luminescent Cell Viability Assay (Promega, Madison, WI, USA), strictly following the manufacturer's technical bulletin. Briefly, an equal volume of CellTiter-Glo reagent was added to each well, followed by 2 minutes of orbital shaking to induce cell lysis, and 10 minutes of incubation at room temperature to stabilize the luminescent signal. Luminescence, which correlates with intracellular ATP levels, was recorded using a Tecan Infinite® M1000 plate reader.

All experiments were performed in triplicate and error bars are standard deviations.

Dose–response curves and IC_{50} values were calculated using nonlinear regression in GraphPad Prism 8 software. An ATP standard curve was included to confirm assay linearity and performance under our experimental conditions.

4 NMR Spectra

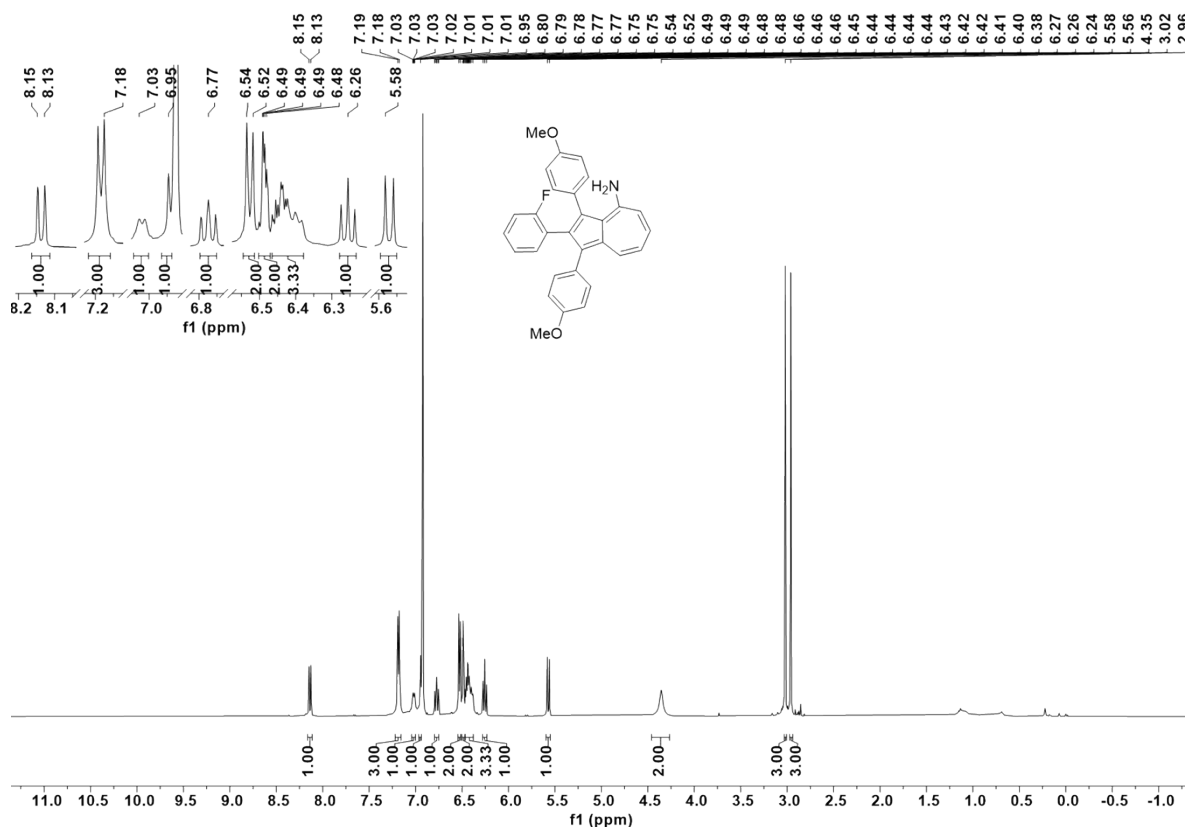


Figure S1. $^1\text{H}\{^{19}\text{F}\}$ NMR Spectrum (500 MHz, C_6D_6 , 295 K) of 4a.

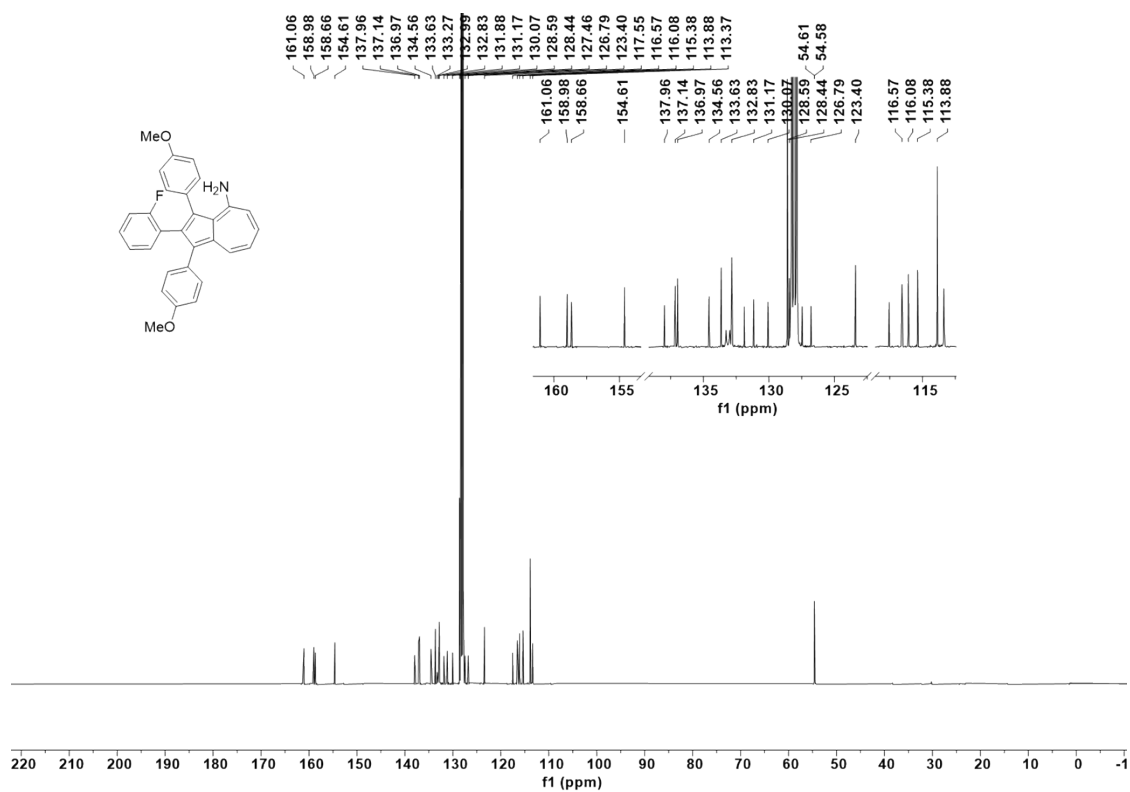


Figure S2. $^{13}\text{C}\{^{19}\text{F}, ^1\text{H}\}$ NMR Spectrum (126 MHz, C_6D_6 , 295 K) of 4a.

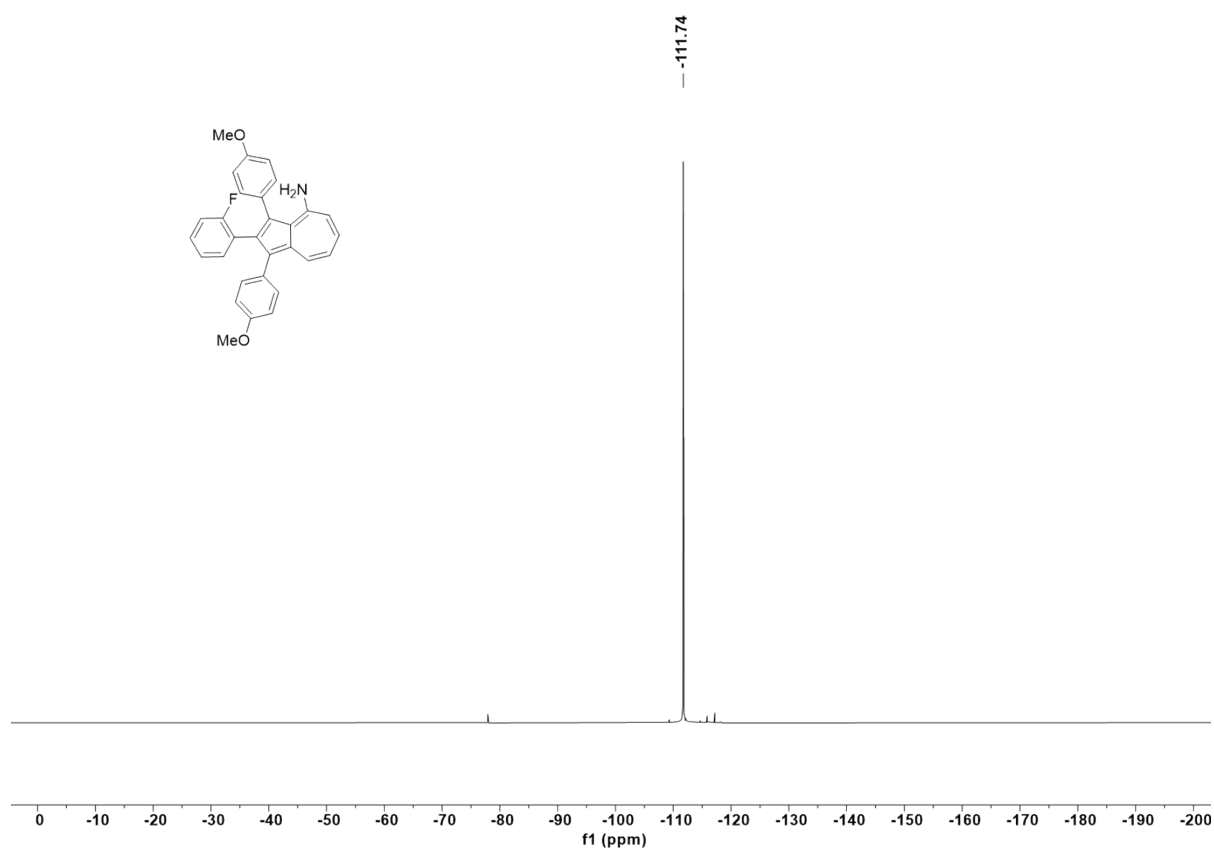


Figure S3. $^{19}\text{F}\{^1\text{H}\}$ NMR Spectrum (471 MHz, C_6D_6 , 295 K) of **4a**.

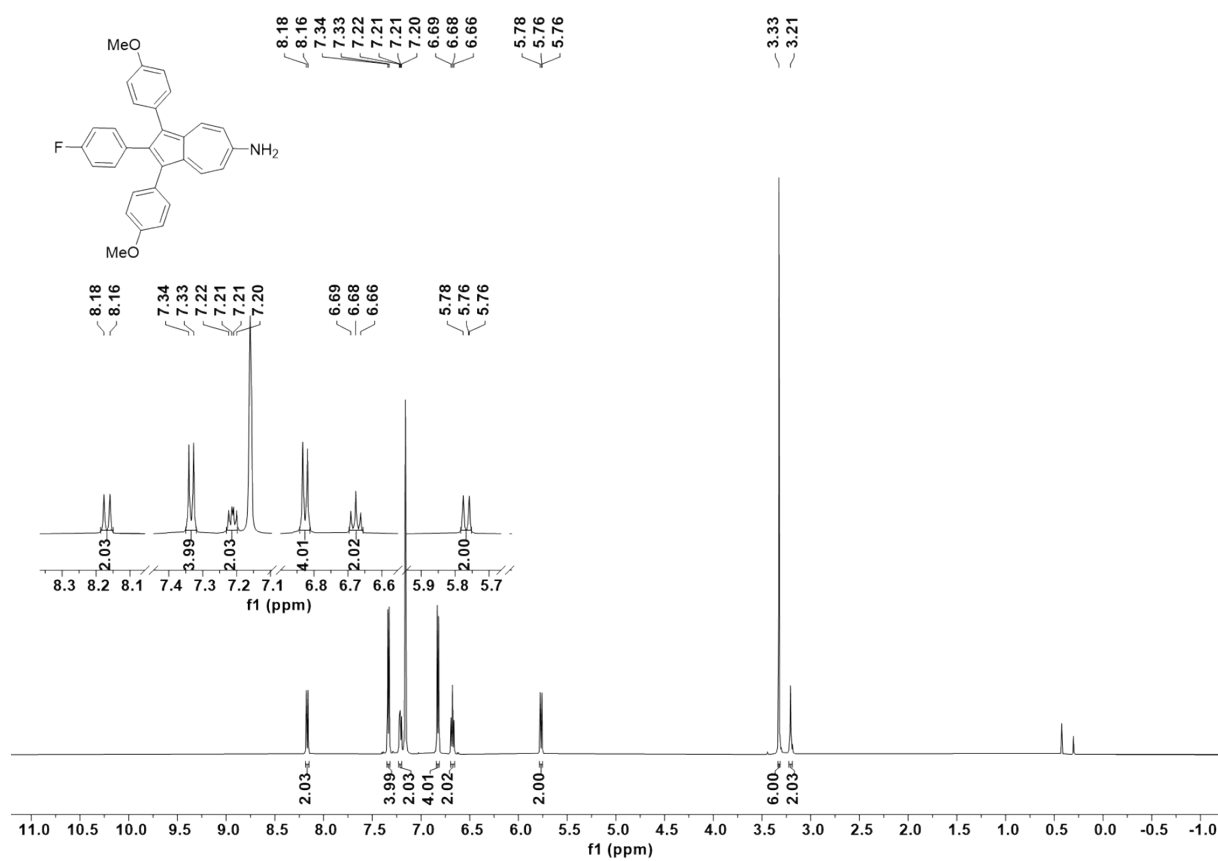


Figure S4. $^1\text{H}\{^{19}\text{F}\}$ NMR Spectrum (600 MHz, C_6D_6 , 295 K) of **4b**.

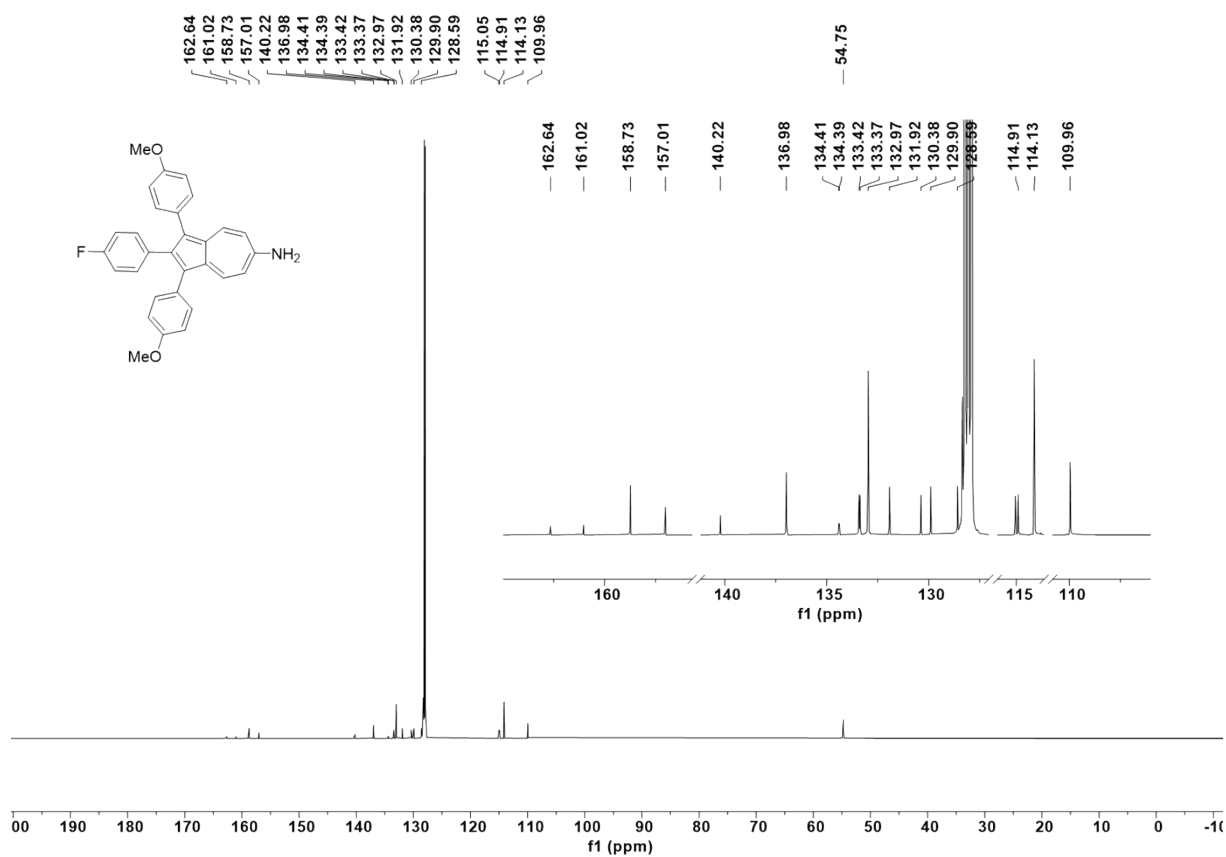


Figure S5. $^{13}\text{C}\{^{19}\text{F}, ^1\text{H}\}$ NMR Spectrum (151 MHz, C_6D_6 , 295 K) of **4b**.

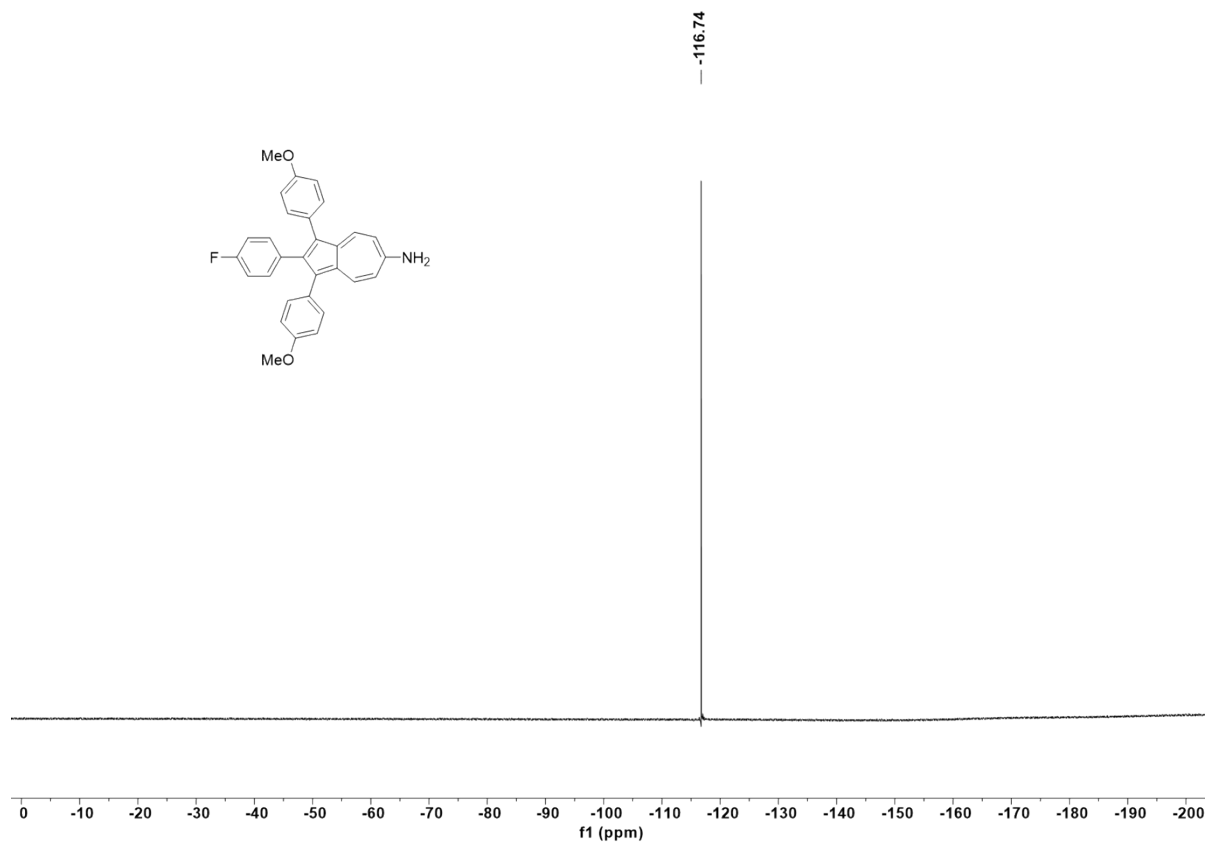


Figure S6. $^{19}\text{F}\{^1\text{H}\}$ NMR Spectrum (283 MHz, C_6D_6 , 295 K) of **4b**.

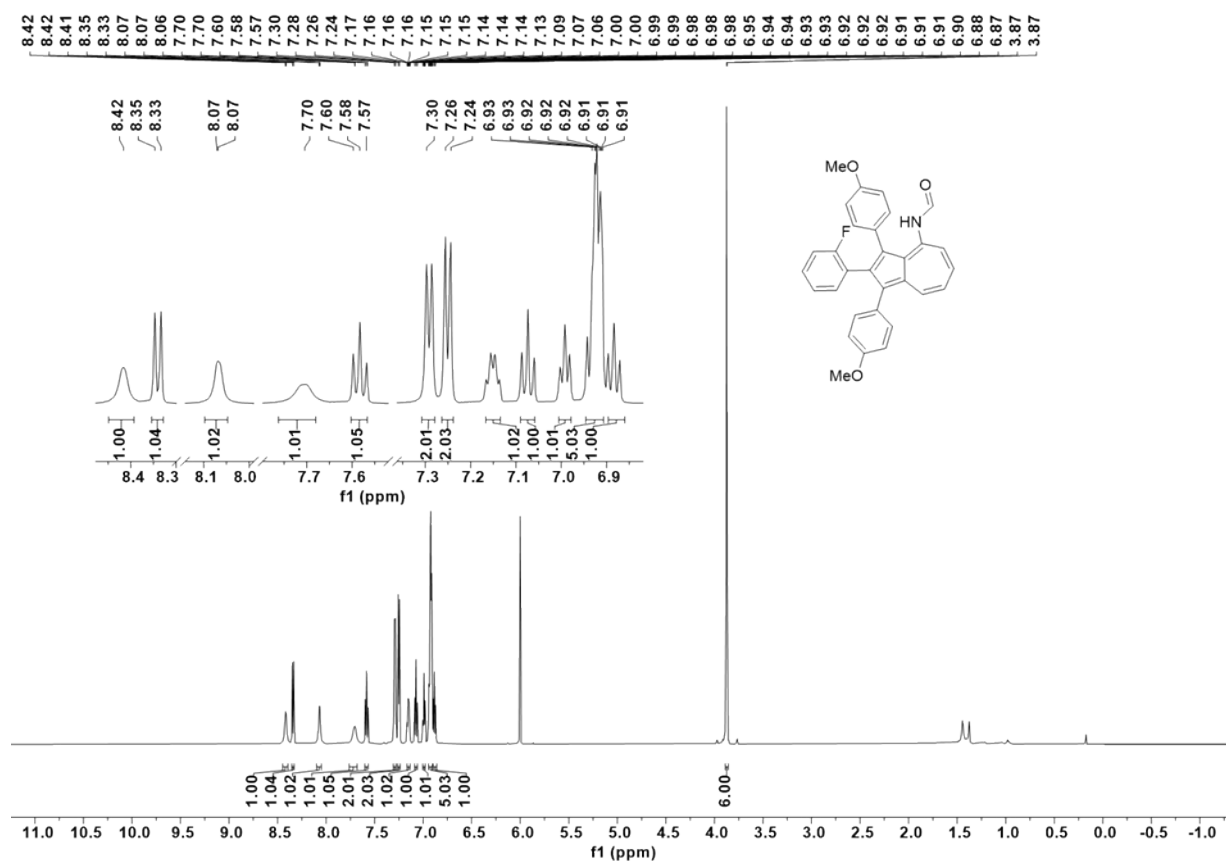


Figure S7. $^1\text{H}\{^{19}\text{F}\}$ NMR Spectrum (700 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 400 K) of **6a**.

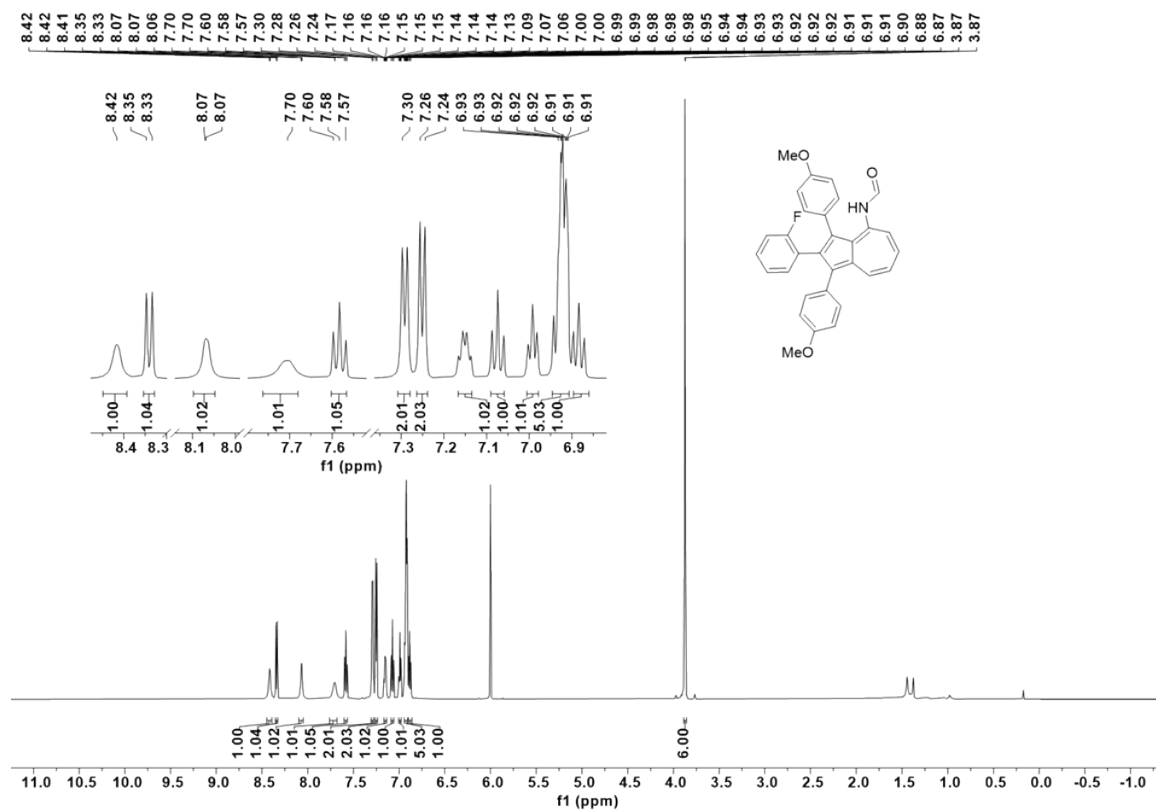


Figure S8. $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum (176 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 400 K) of **6a**.

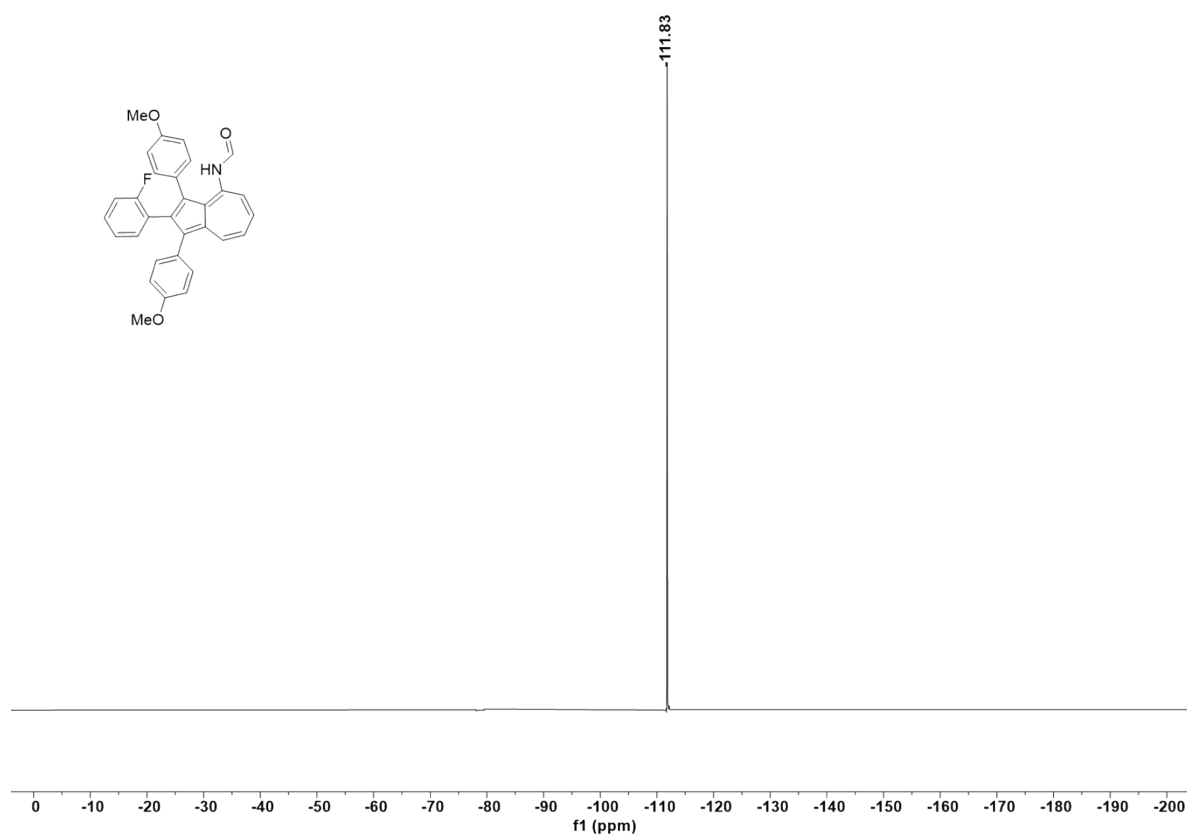


Figure S9. $^{19}\text{F}\{^1\text{H}\}$ NMR Spectrum (471 MHz, C_6D_6 , 295 K) of **6a**.

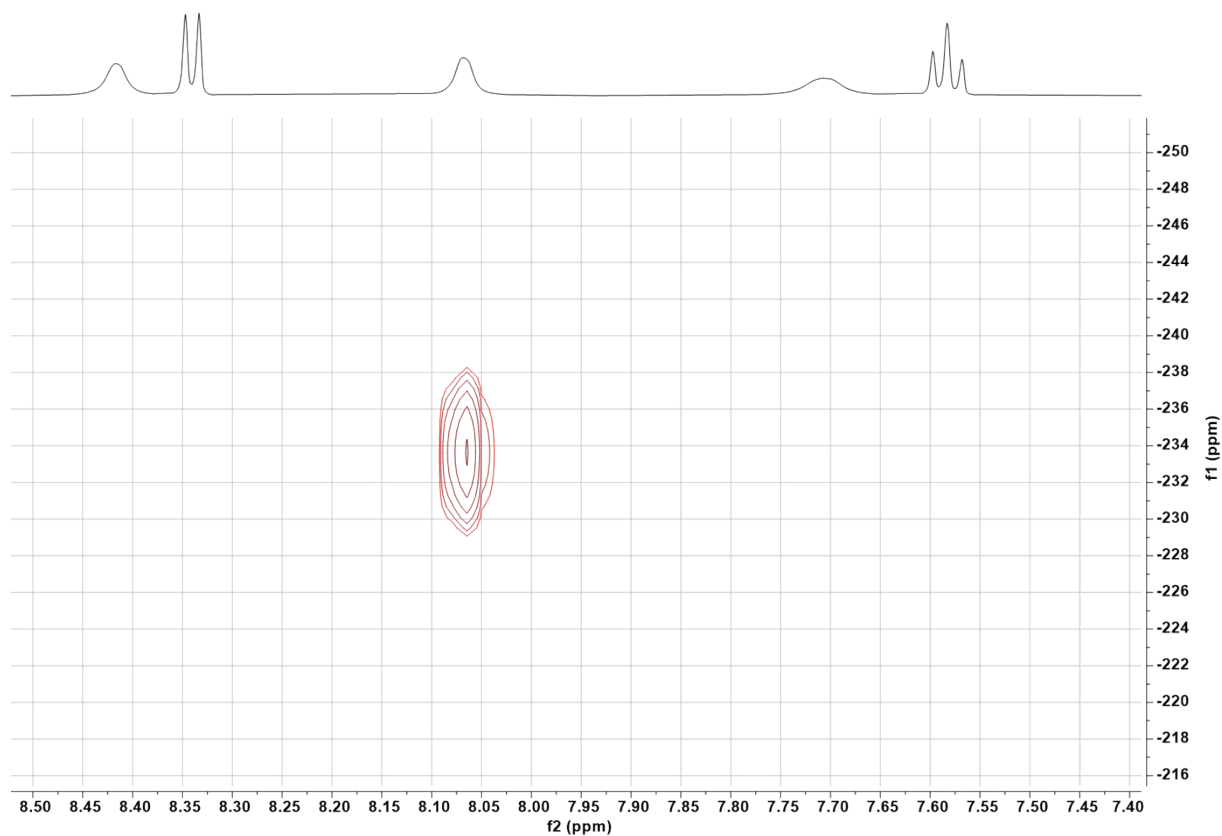


Figure S10. ^1H , ^{15}N -HSQC Spectrum of **6a**.

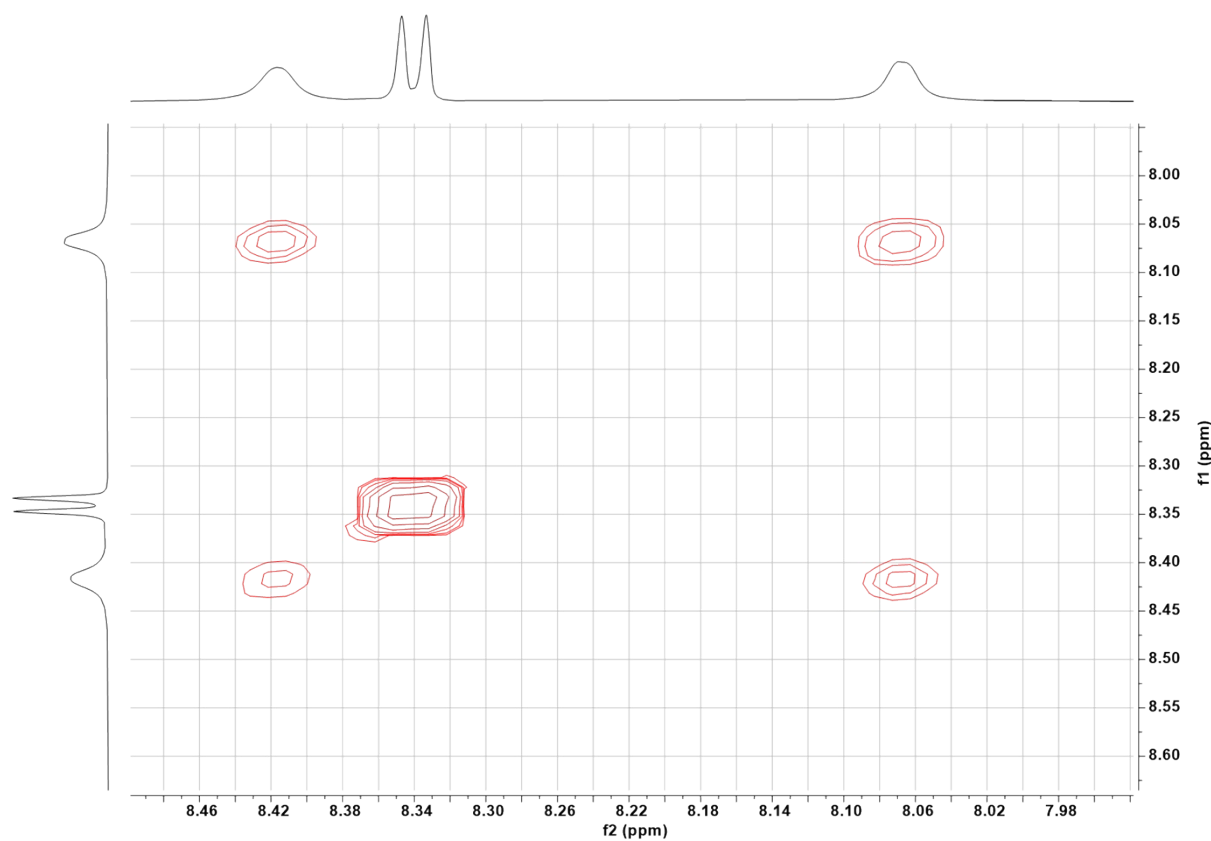


Figure S11. ^1H , ^1H COSY Spectrum of **6a**.

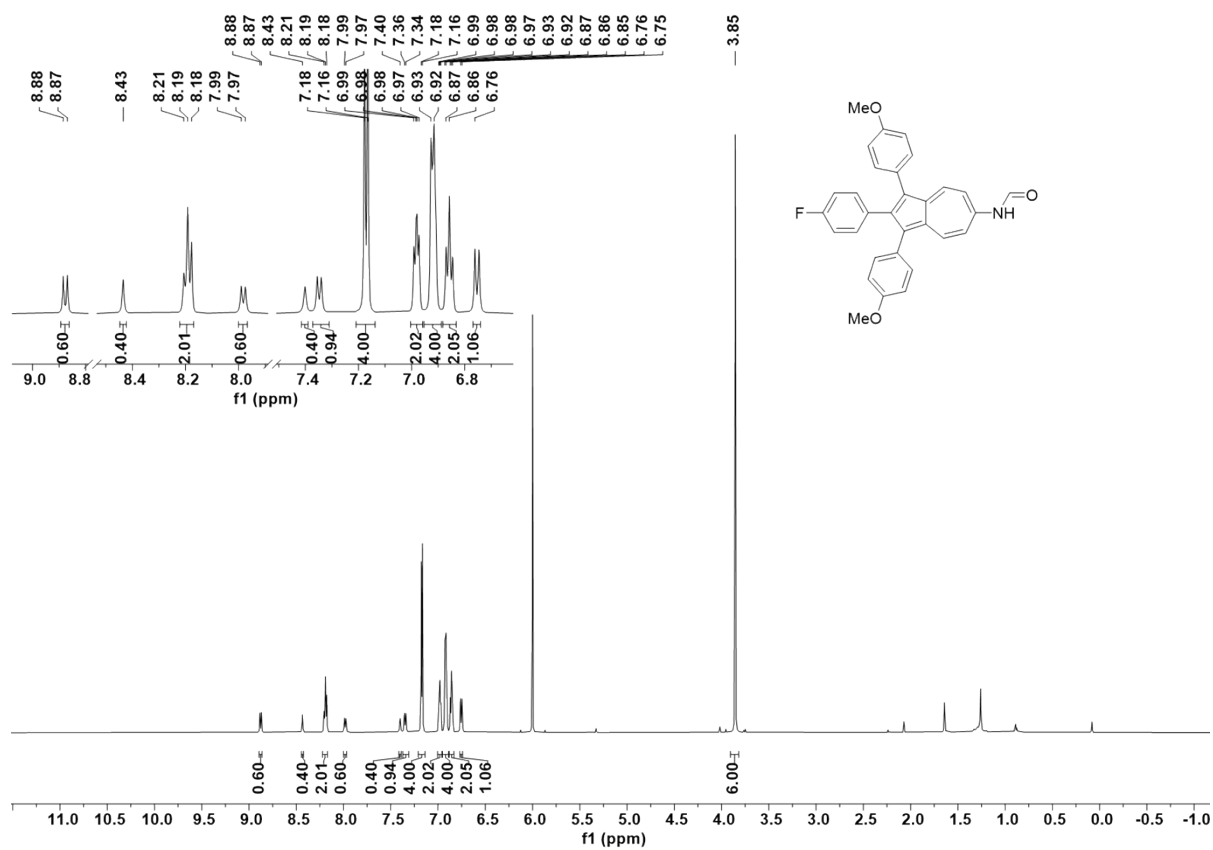


Figure S12. $^1\text{H}\{^{19}\text{F}\}$ NMR Spectrum (700 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 295 K) of **6b**.

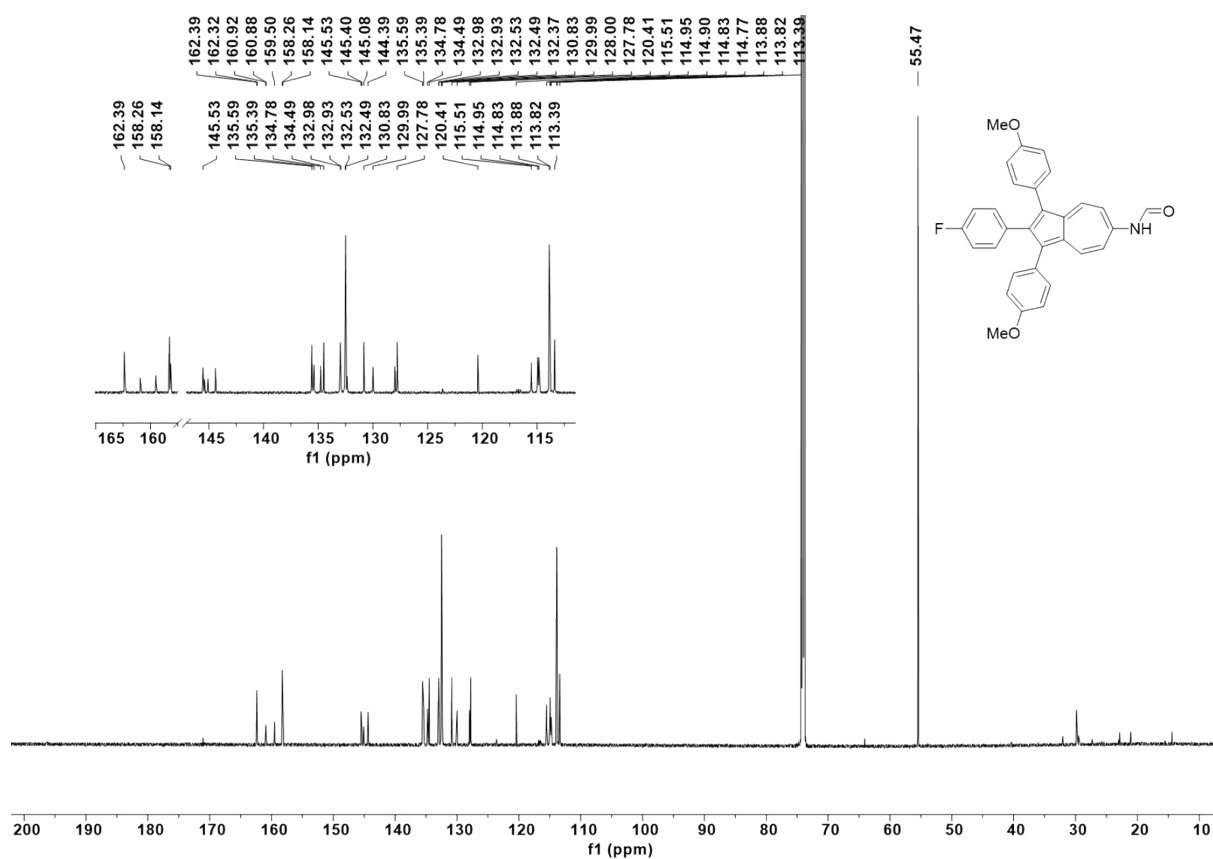


Figure S13. $^{13}\text{C}\{^{19}\text{F}, ^1\text{H}\}$ NMR Spectrum (151 MHz, CD_2Cl_2 , 295 K) of **6b**.

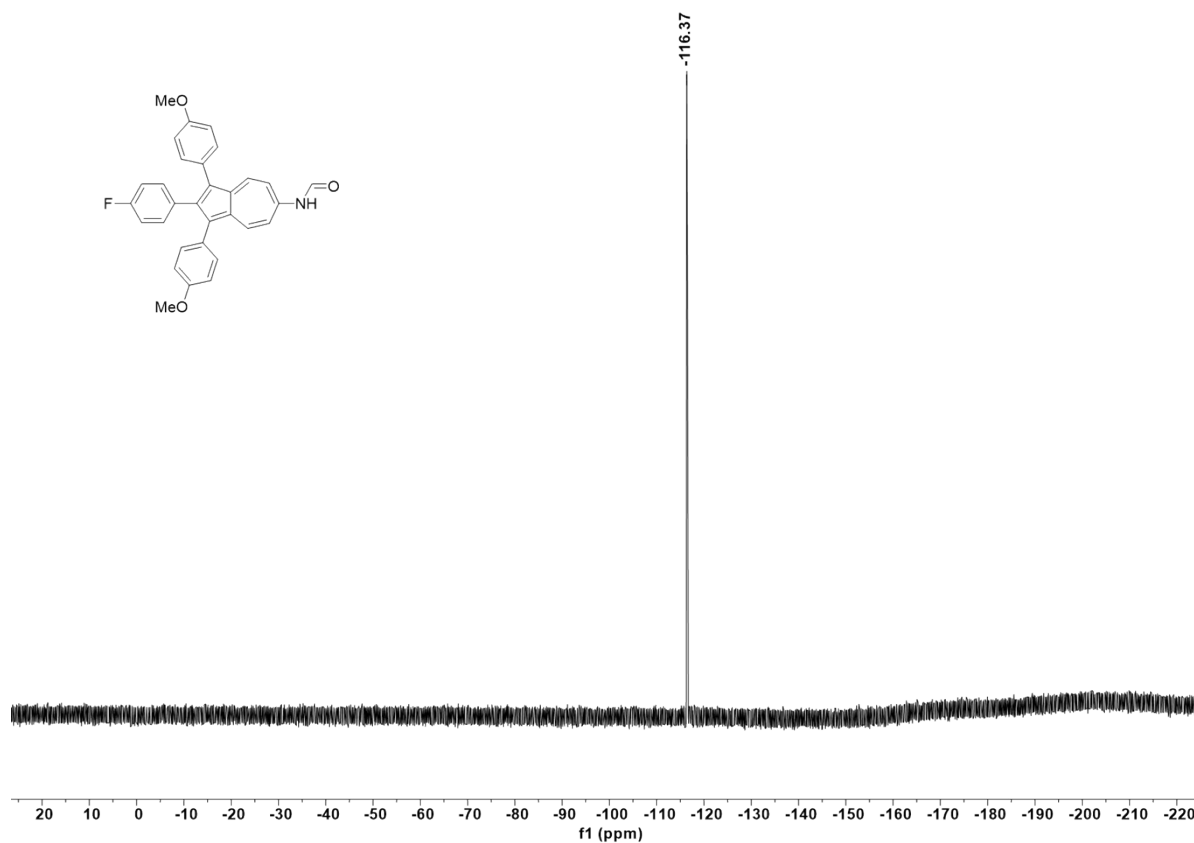


Figure S14. $^{19}\text{F}\{^1\text{H}\}$ NMR Spectrum (283 MHz, CD_2Cl_2 , 295 K) of **6b**.

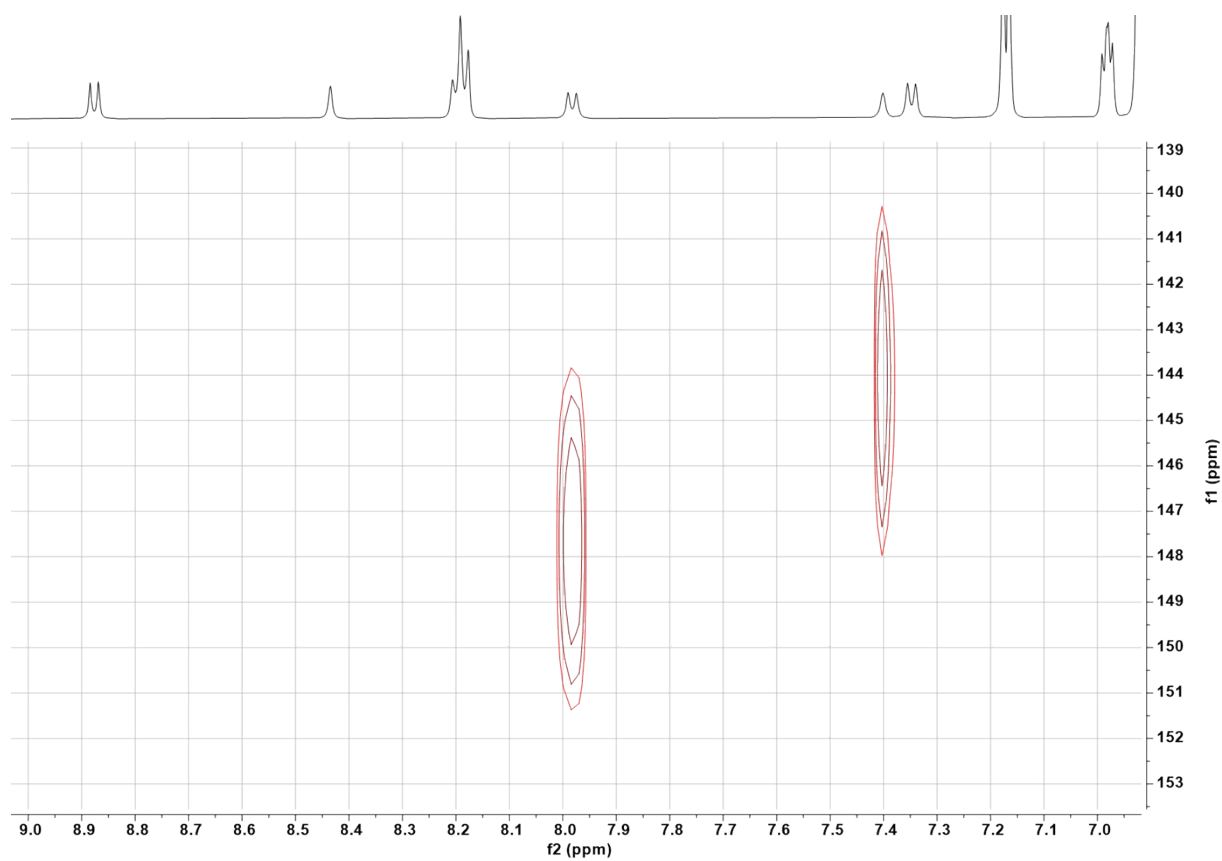


Figure S15. ^1H , ^{15}N -HSQC Spectrum of **6b**.

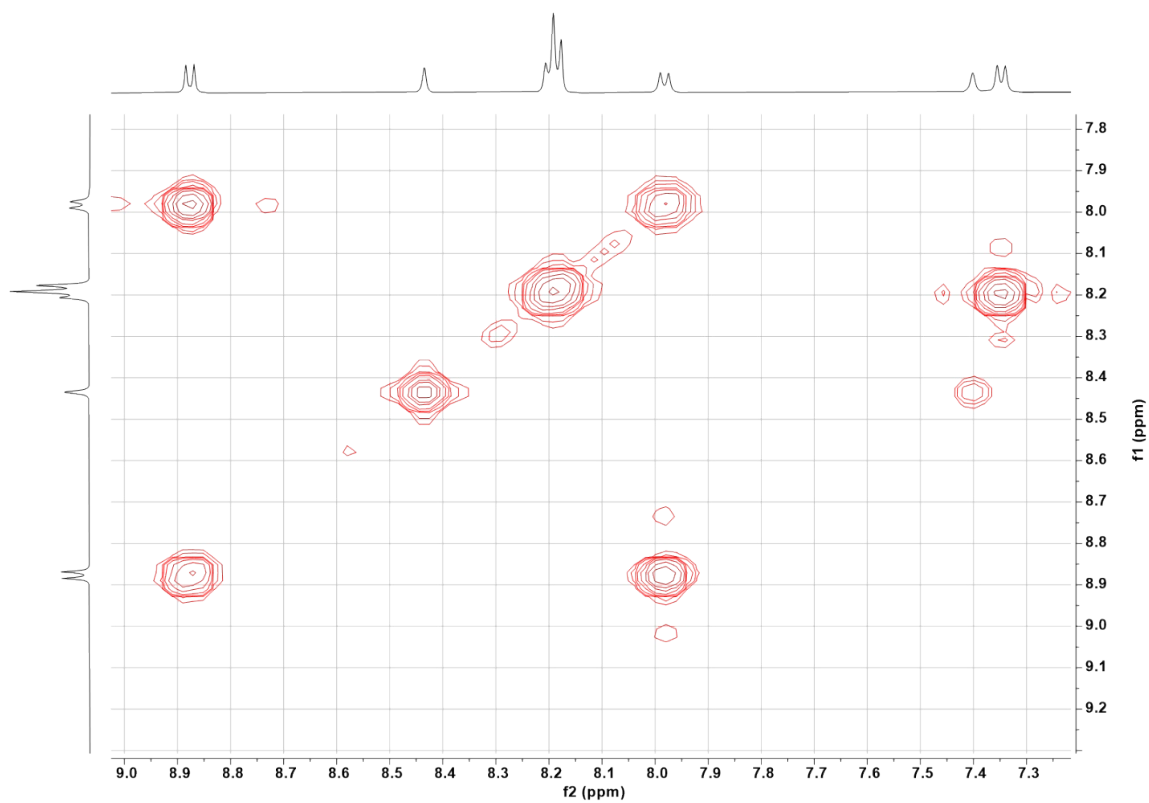


Figure S16. ^1H , ^1H -COSY Spectrum of **6b**.

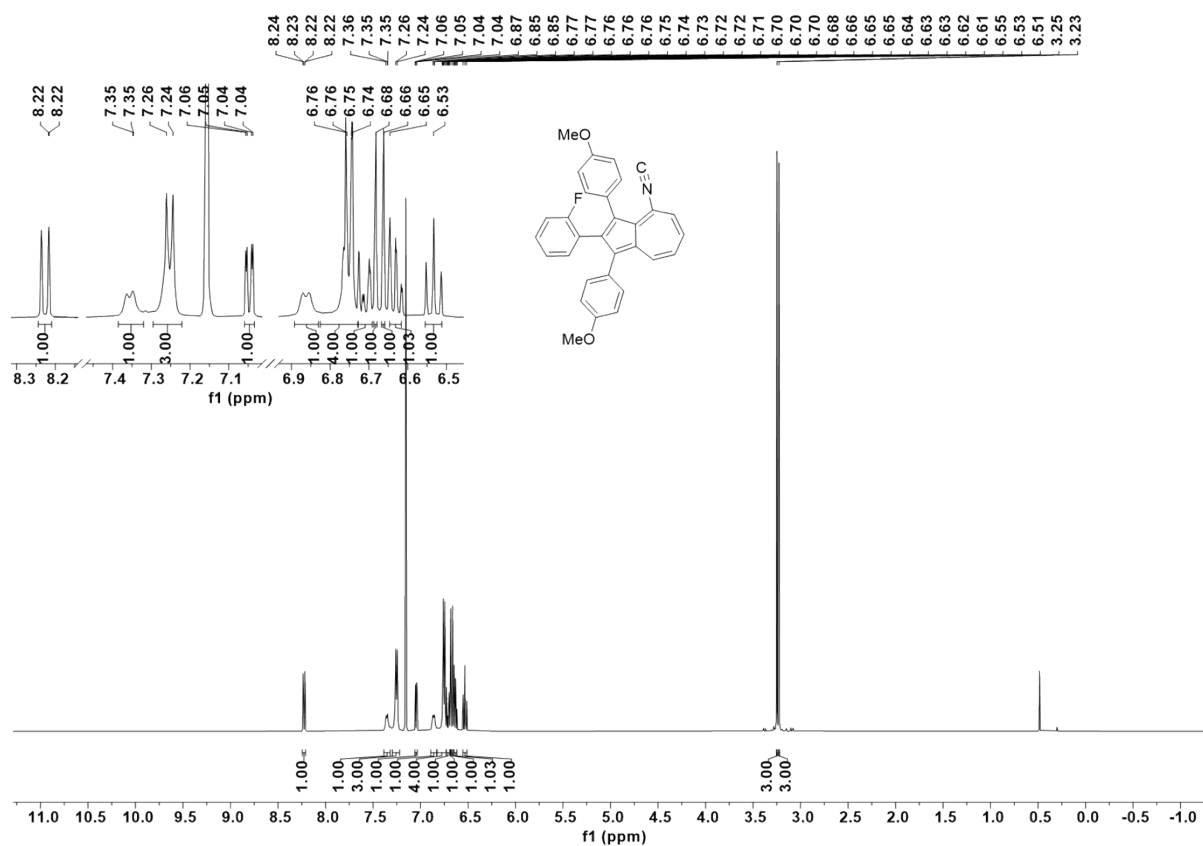


Figure S17. $^1\text{H}\{^{19}\text{F}\}$ NMR Spectrum (500 MHz, C_6D_6 , 295 K) of **10a**.

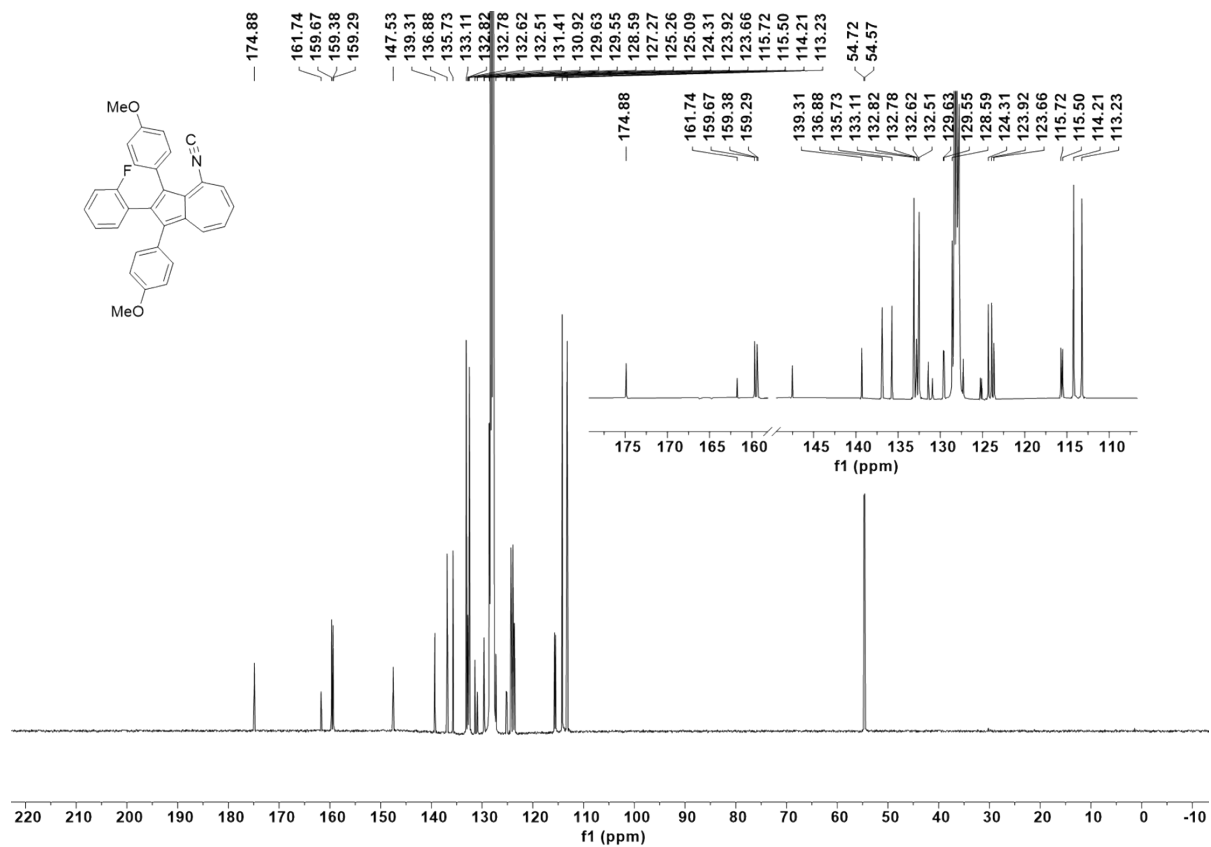


Figure S18. $^{13}\text{C}\{^{19}\text{F}, ^1\text{H}\}$ NMR Spectrum (101 MHz, C_6D_6 , 295 K) of **10a**.

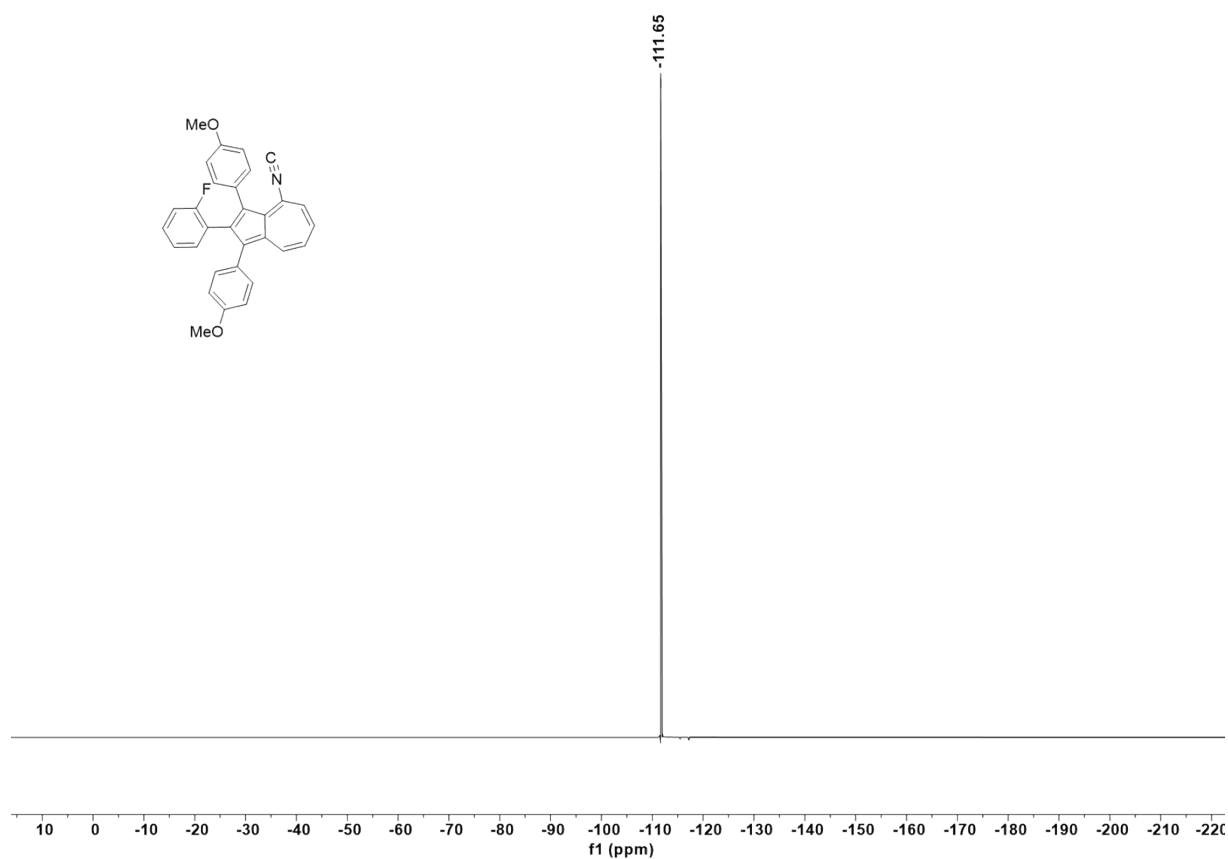


Figure S19. $^{19}\text{F}\{^1\text{H}\}$ NMR Spectrum (471 MHz, C_6D_6 , 295 K) of **10a**.

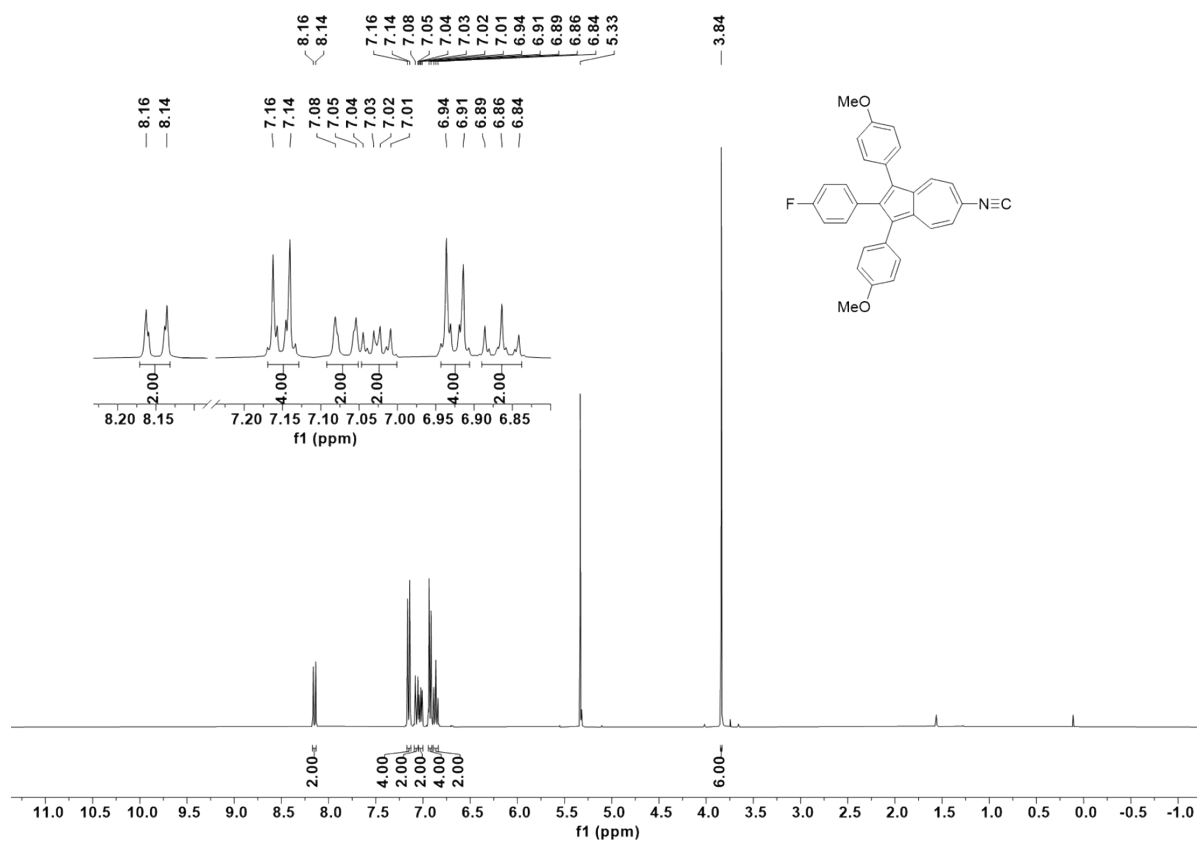


Figure S20. $^1\text{H}\{^{19}\text{F}\}$ NMR Spectrum (400 MHz, CD_2Cl_2 , 295 K) of **10b**.

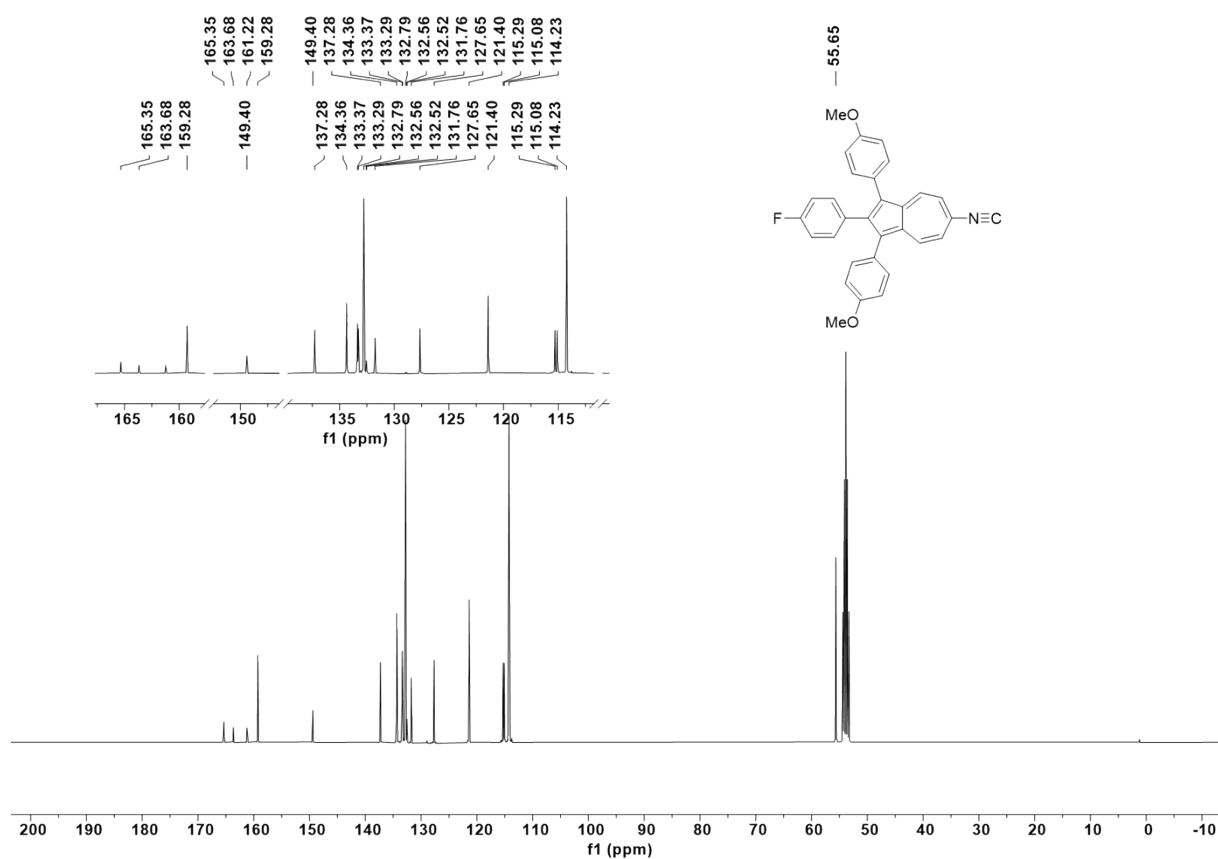


Figure S21. $^{13}\text{C}\{^{19}\text{F}, ^1\text{H}\}$ NMR Spectrum (101 MHz, CD_2Cl_2 , 295 K) of **10b**.

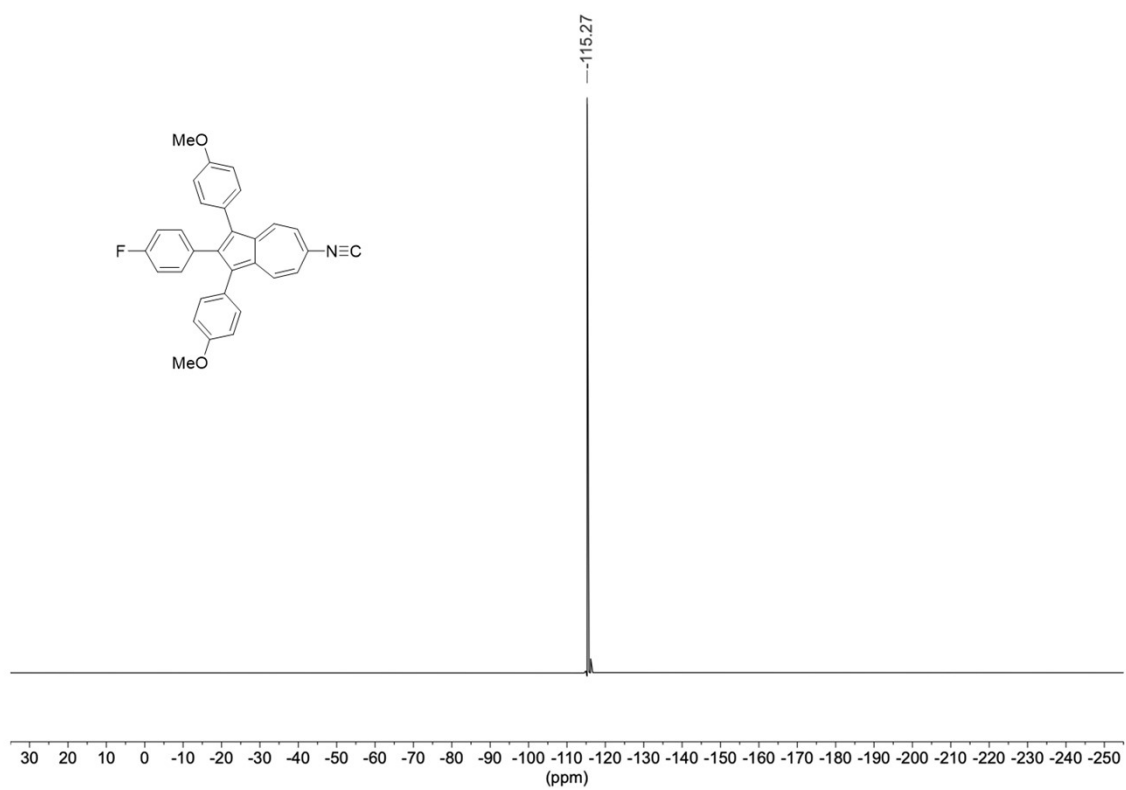


Figure S22. $^{19}\text{F}\{^1\text{H}\}$ NMR Spectrum (283 MHz, CD_2Cl_2 , 298 K) of **10b**.

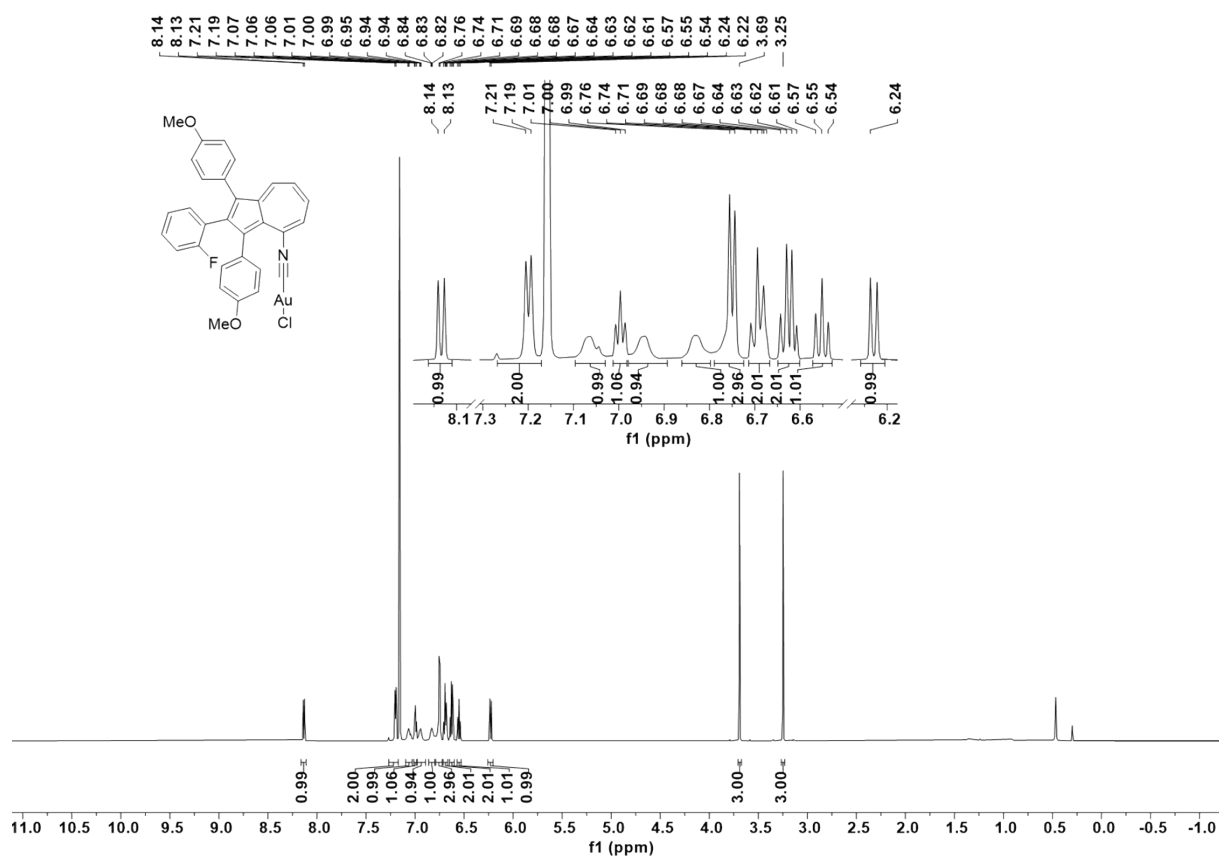


Figure S23. $^1\text{H}\{^{19}\text{F}\}$ NMR Spectrum (700 MHz, C_6D_6 , 295 K) of 12a.

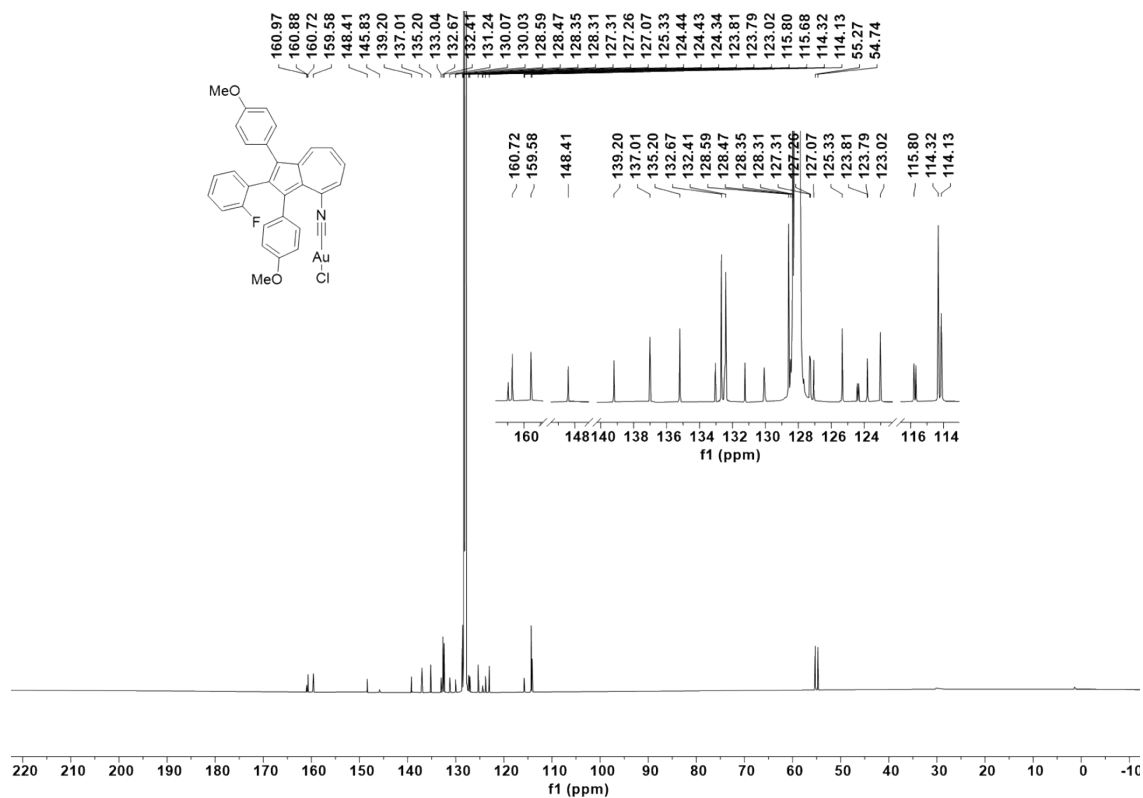


Figure S24. $^{13}\text{C}\{^{19}\text{F}, ^1\text{H}\}$ NMR Spectrum (176 MHz, C_6D_6 , 295 K) of 12a.

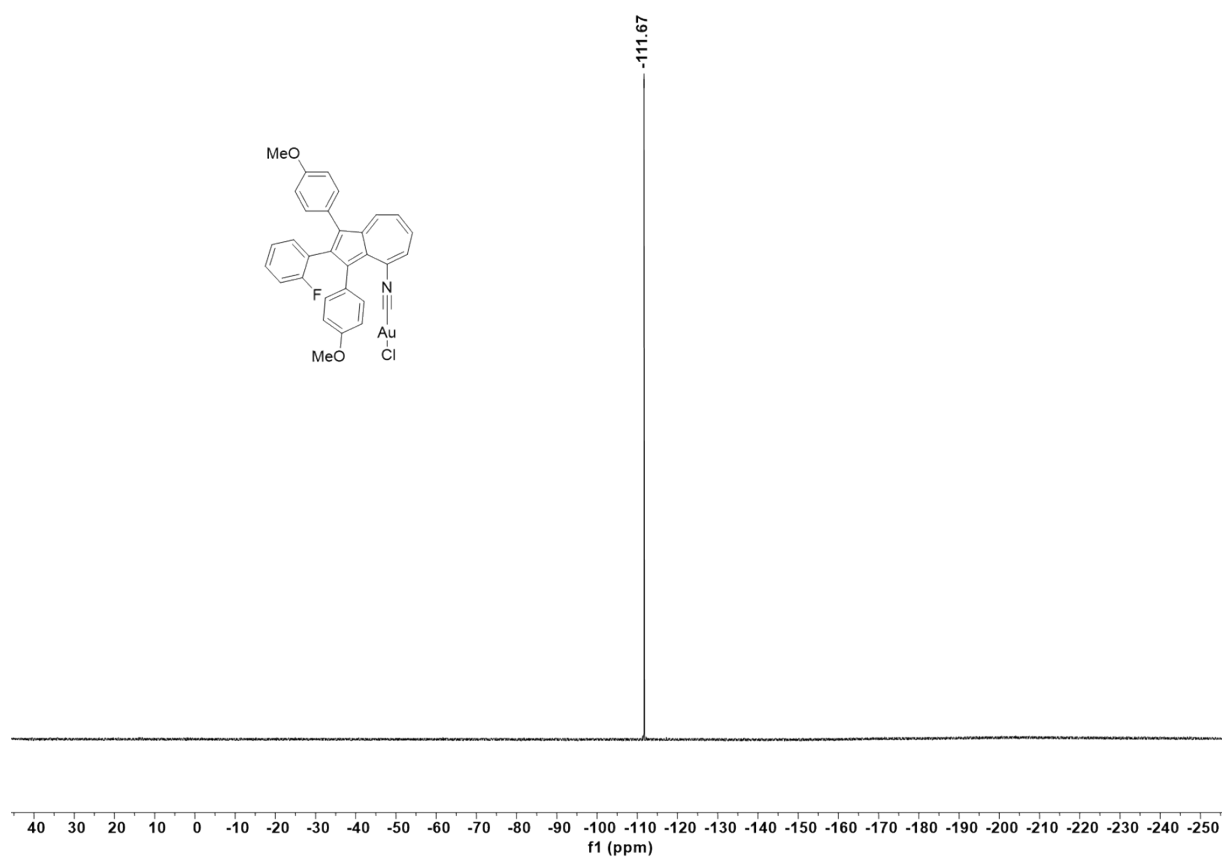


Figure S25. $^{19}\text{F}\{^1\text{H}\}$ NMR Spectrum (283 MHz, C_6D_6 , 295 K) of 12a.

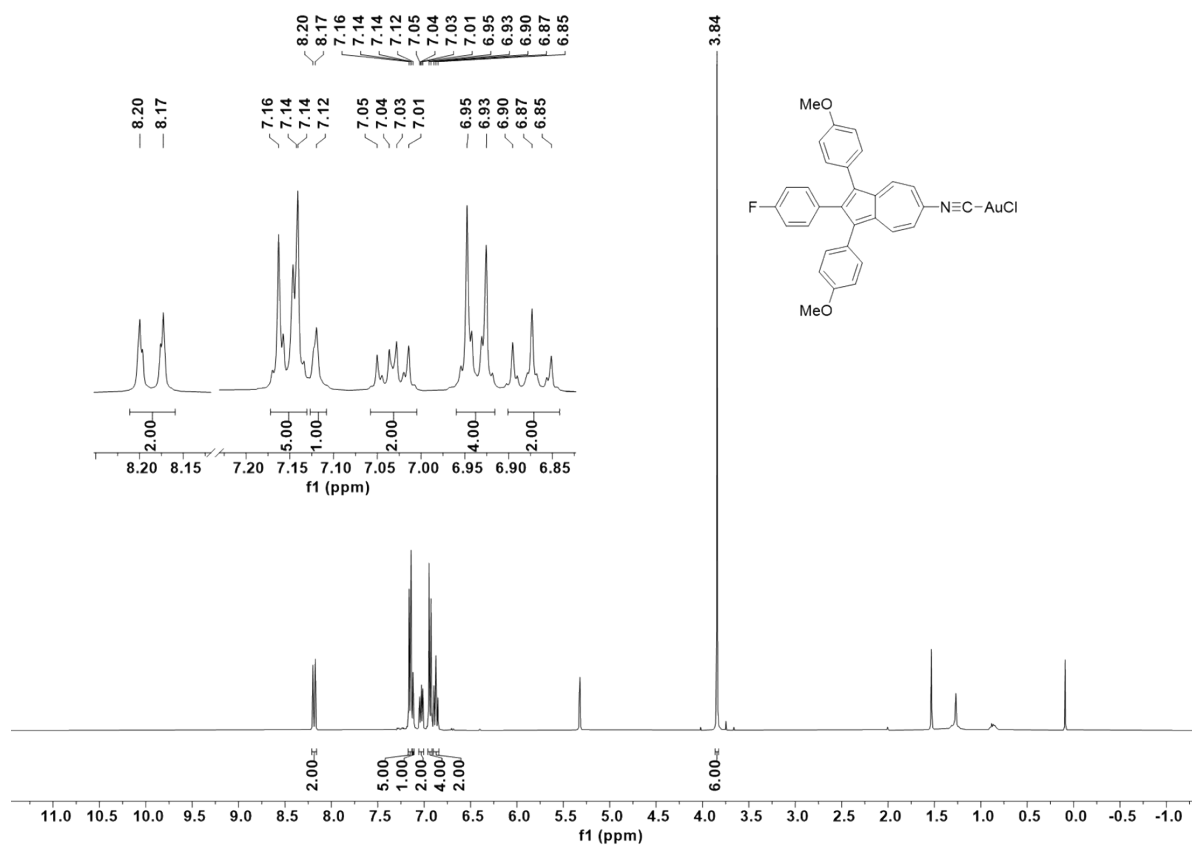


Figure S26. $^1\text{H}\{^{19}\text{F}\}$ NMR Spectrum (400 MHz, CD_2Cl_2 , 295 K) of 12b.

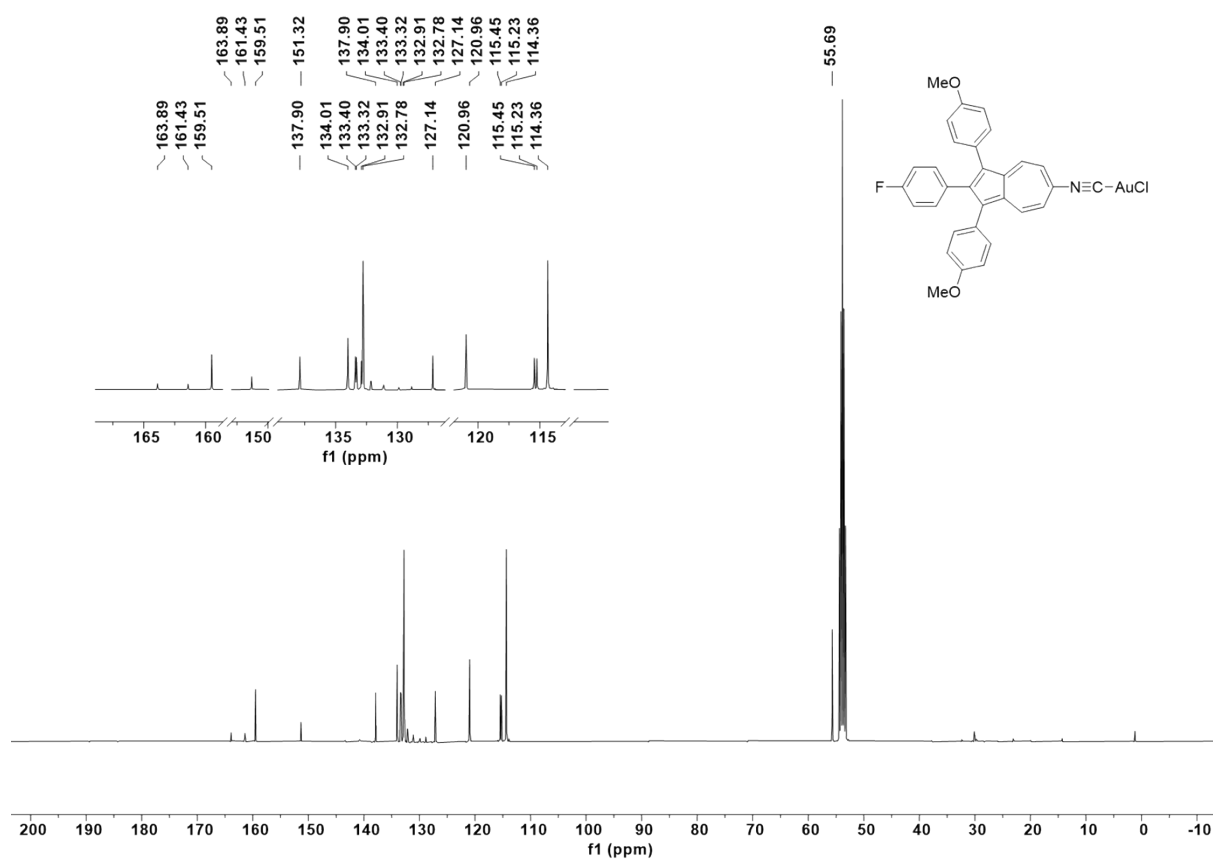


Figure S27. $^{13}\text{C}\{^{19}\text{F}, ^1\text{H}\}$ NMR Spectrum (101 MHz, CD_2Cl_2 , 295 K) of **12b**.

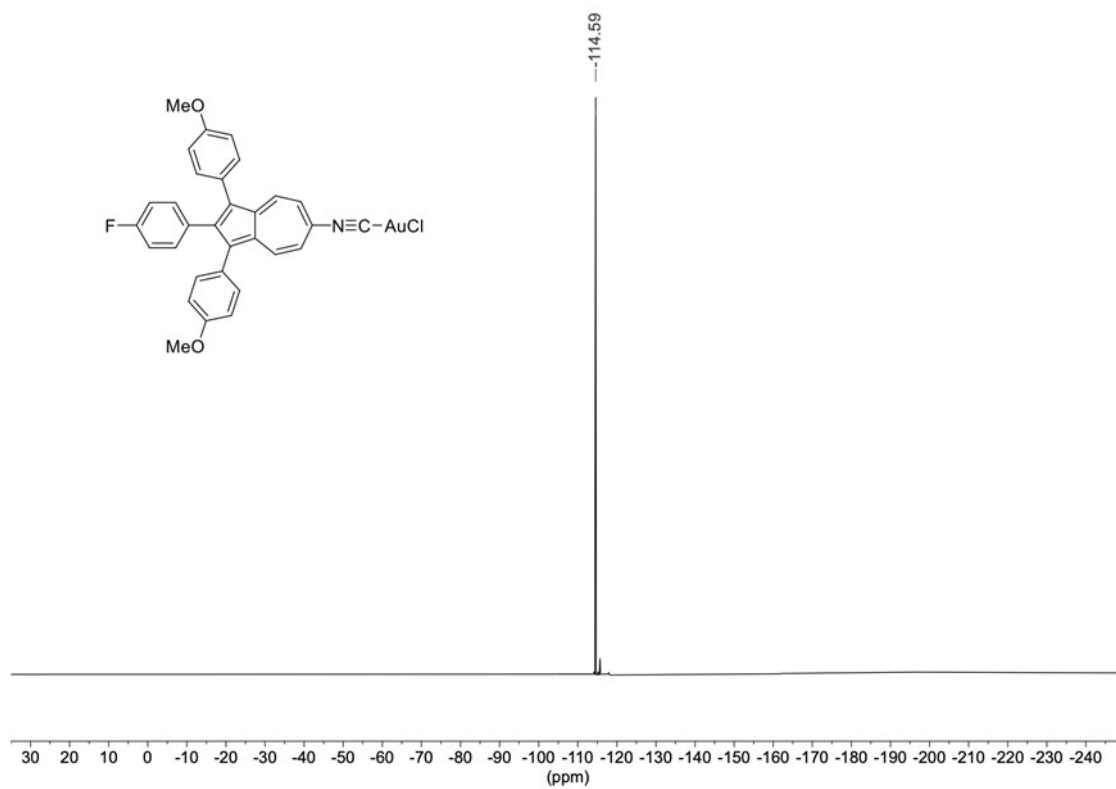
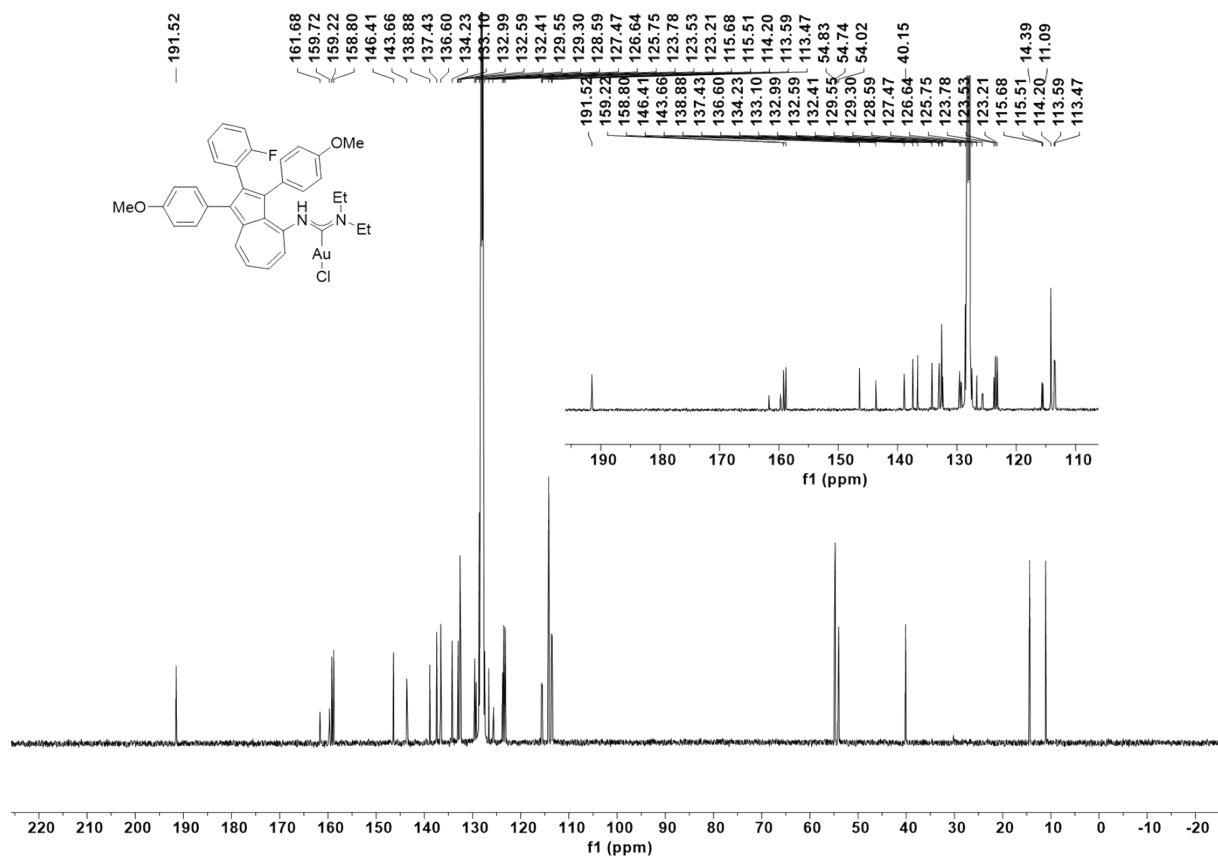
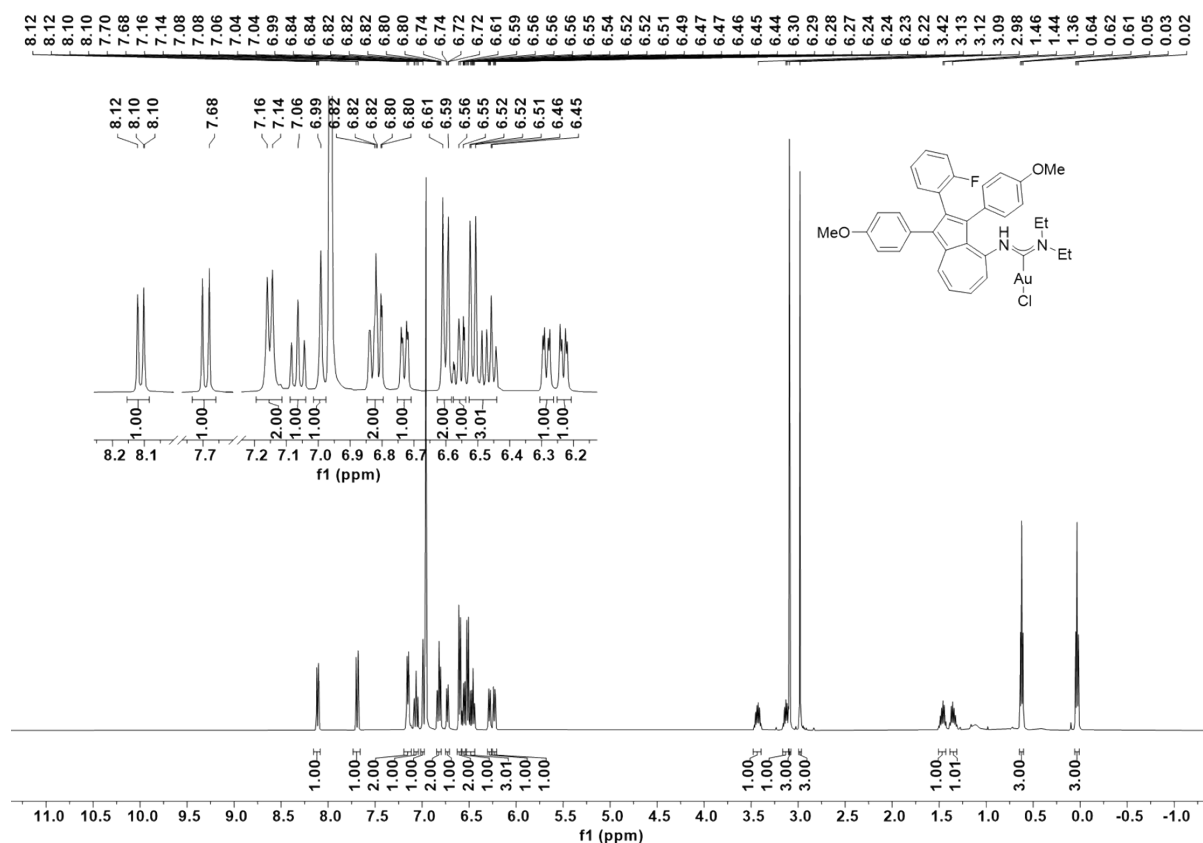


Figure S28. $^{19}\text{F}\{^1\text{H}\}$ NMR Spectrum (283 MHz, CD_2Cl_2 , 298 K) of **12b**.



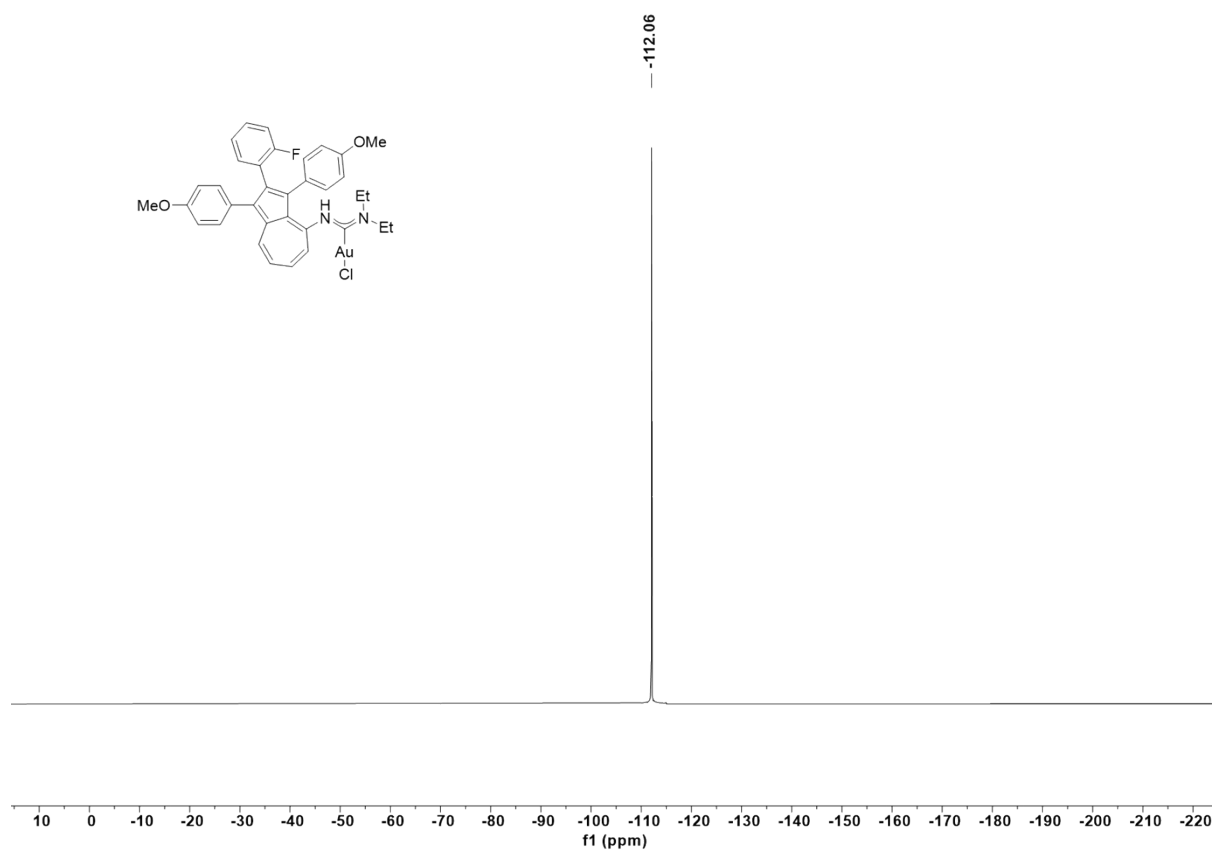


Figure S31. $^{19}\text{F}\{^1\text{H}\}$ NMR Spectrum (471 MHz, C_6D_6 , 295 K) of **14aa**.

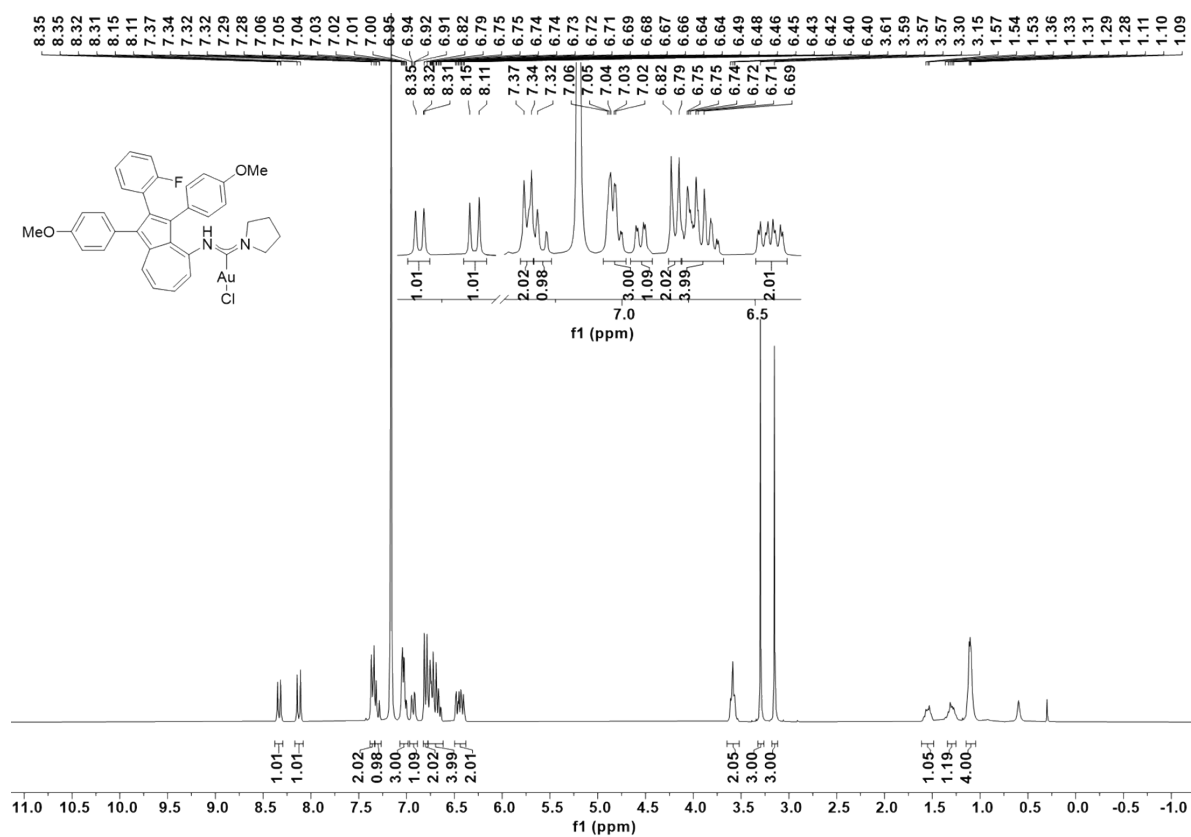


Figure S32. $^1\text{H}\{^{19}\text{F}\}$ NMR Spectrum (301 MHz, C_6D_6 , 295 K) of **14ab**.

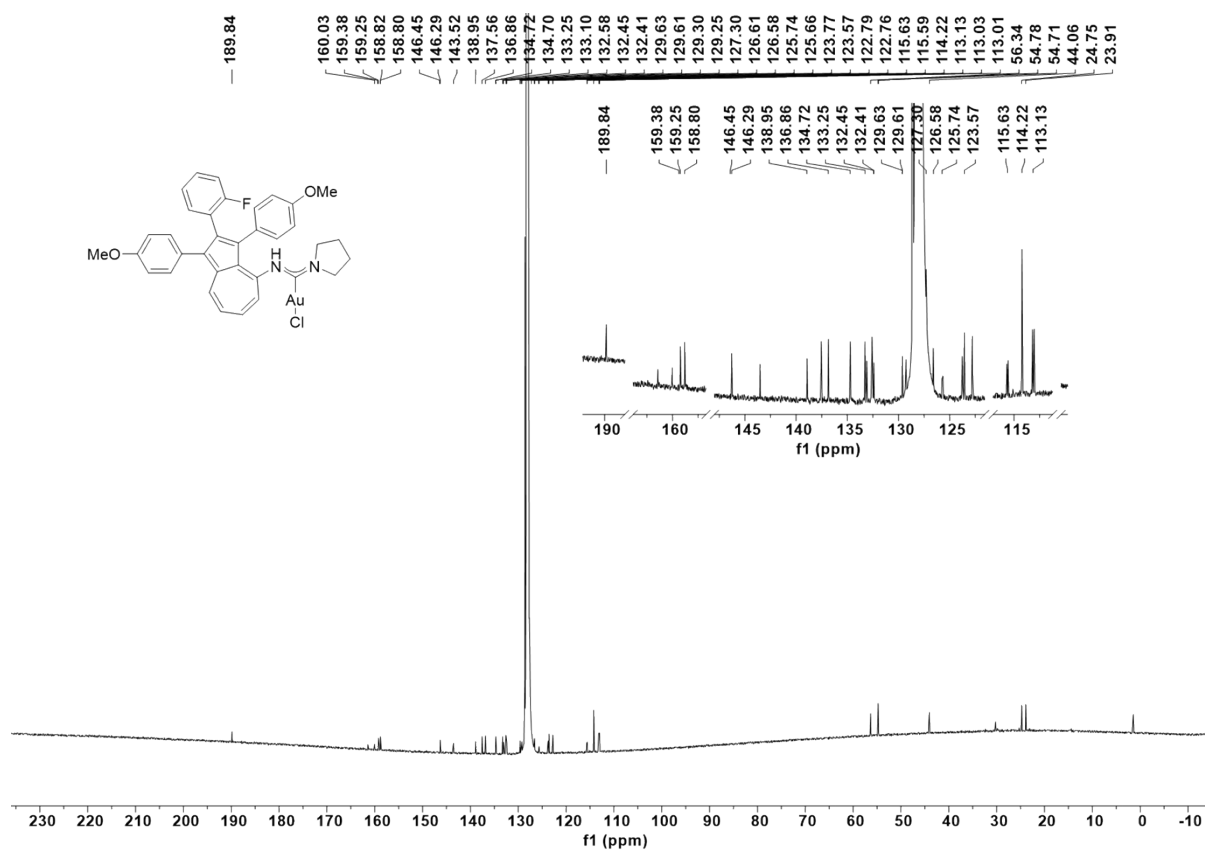


Figure S33. $^{13}\text{C}\{^{19}\text{F}, ^1\text{H}\}$ NMR Spectrum (176 MHz, C_6D_6 , 295 K) of **14ab**.

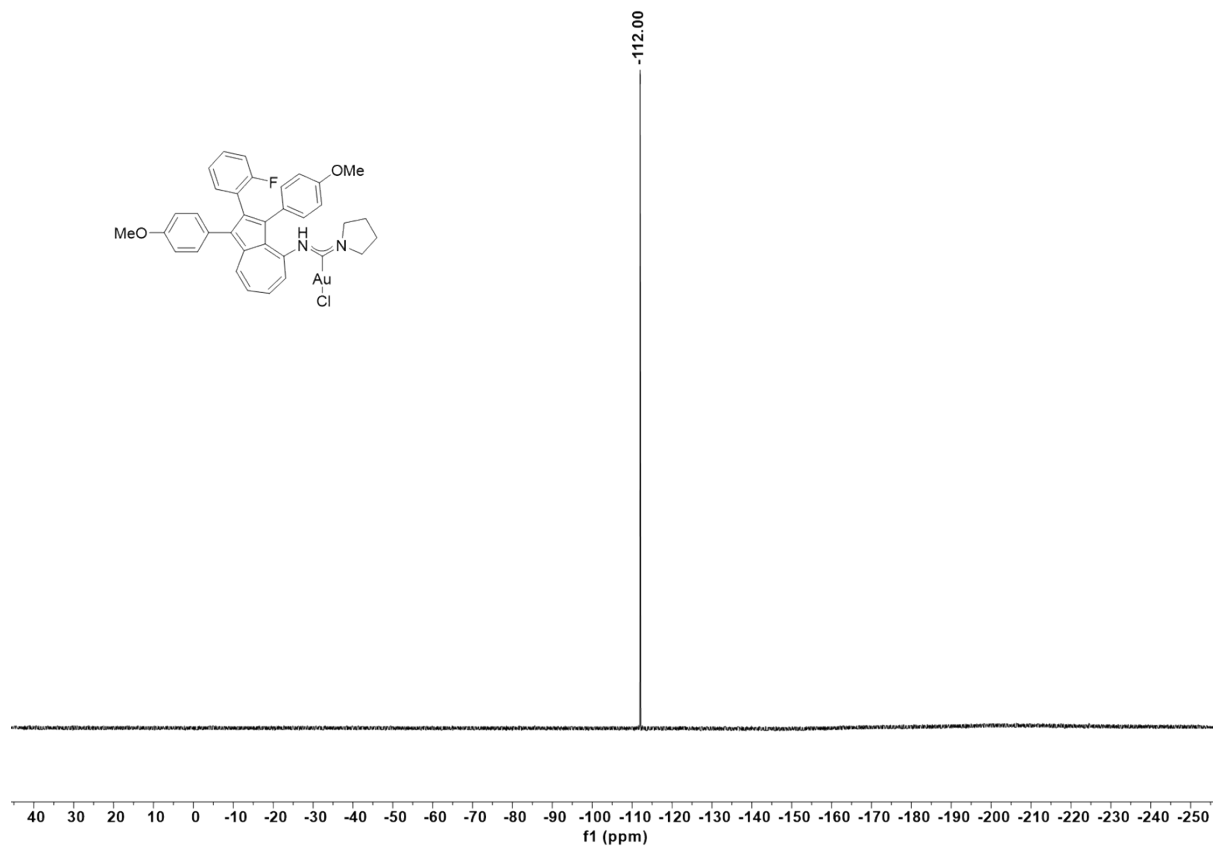


Figure S34. $^{19}\text{F}\{^1\text{H}\}$ NMR Spectrum (283 MHz, C_6D_6 , 295 K) of **14ab**.

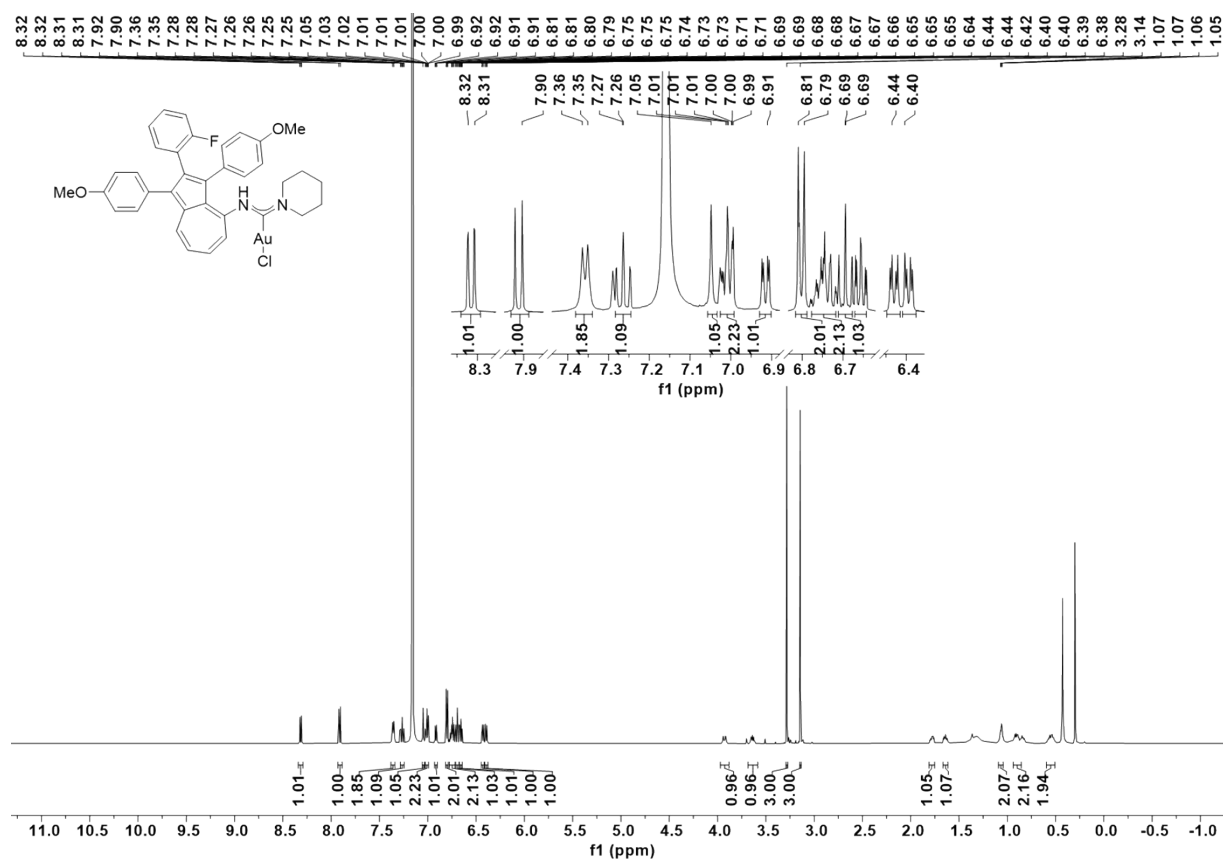


Figure S35. ¹H{¹⁹F} NMR Spectrum (600 MHz, C₆D₆, 295 K) of **14ac**.

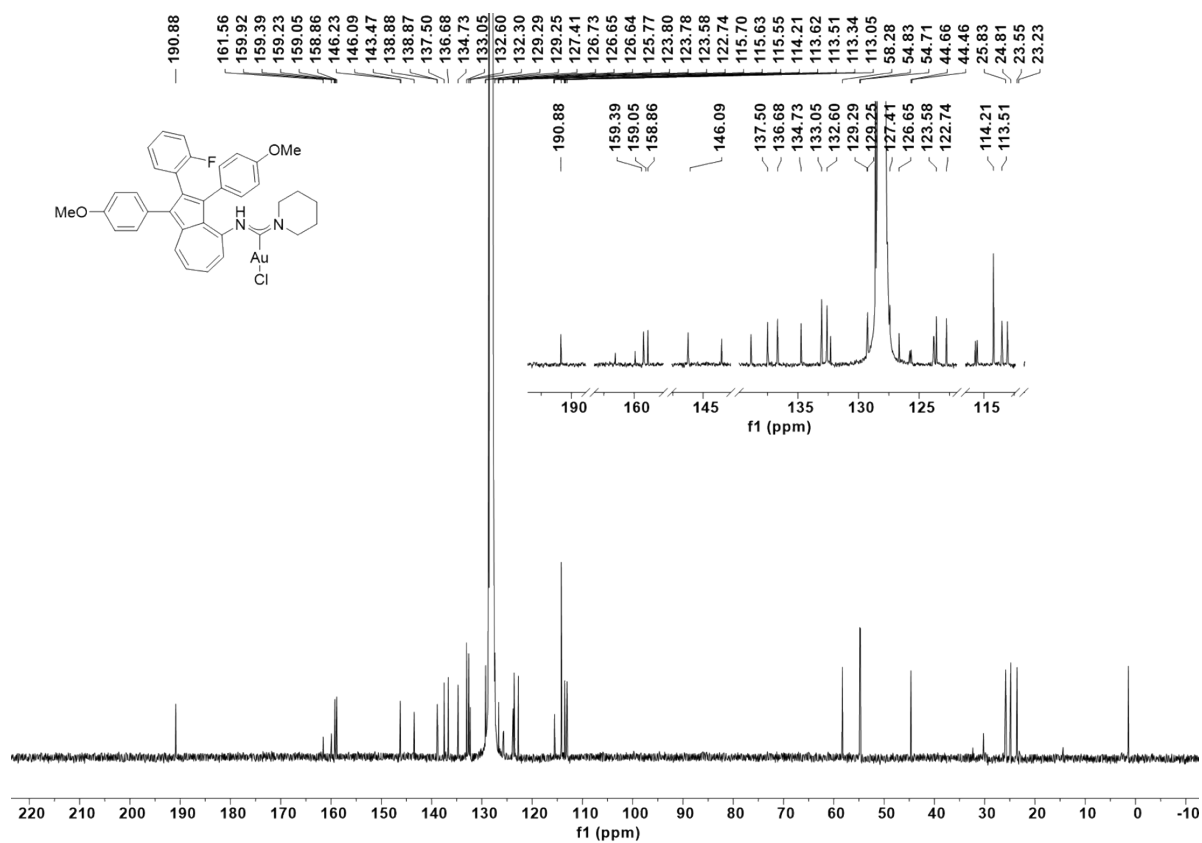


Figure S36. ¹³C{¹⁹F, ¹H} NMR Spectrum (151 MHz, C₆D₆, 295 K) of **14ac**.

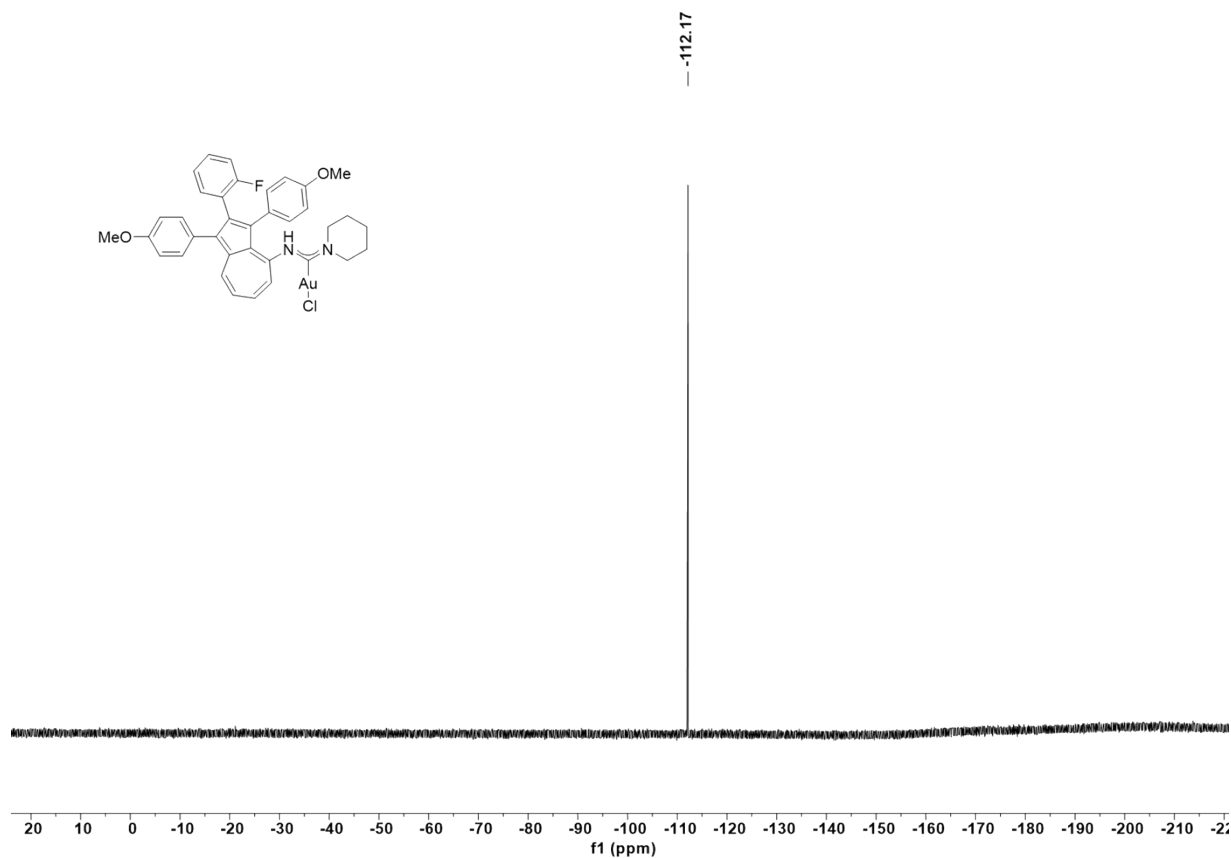


Figure S37. $^{19}\text{F}\{^1\text{H}\}$ NMR Spectrum (283 MHz, C_6D_6 , 295 K) of **14ac**.

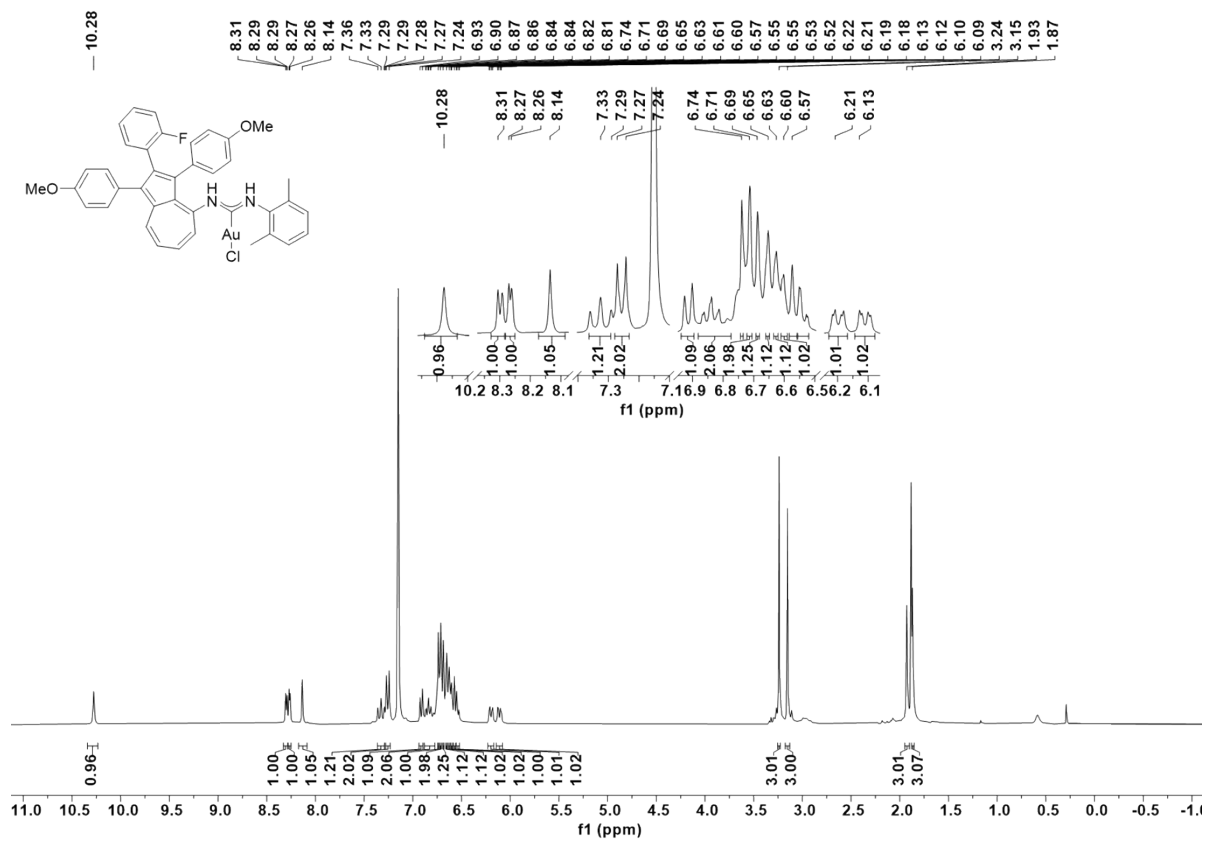


Figure S38. $^1\text{H}\{^{19}\text{F}\}$ NMR Spectrum (301 MHz, C_6D_6 , 295 K) of **14ad**.

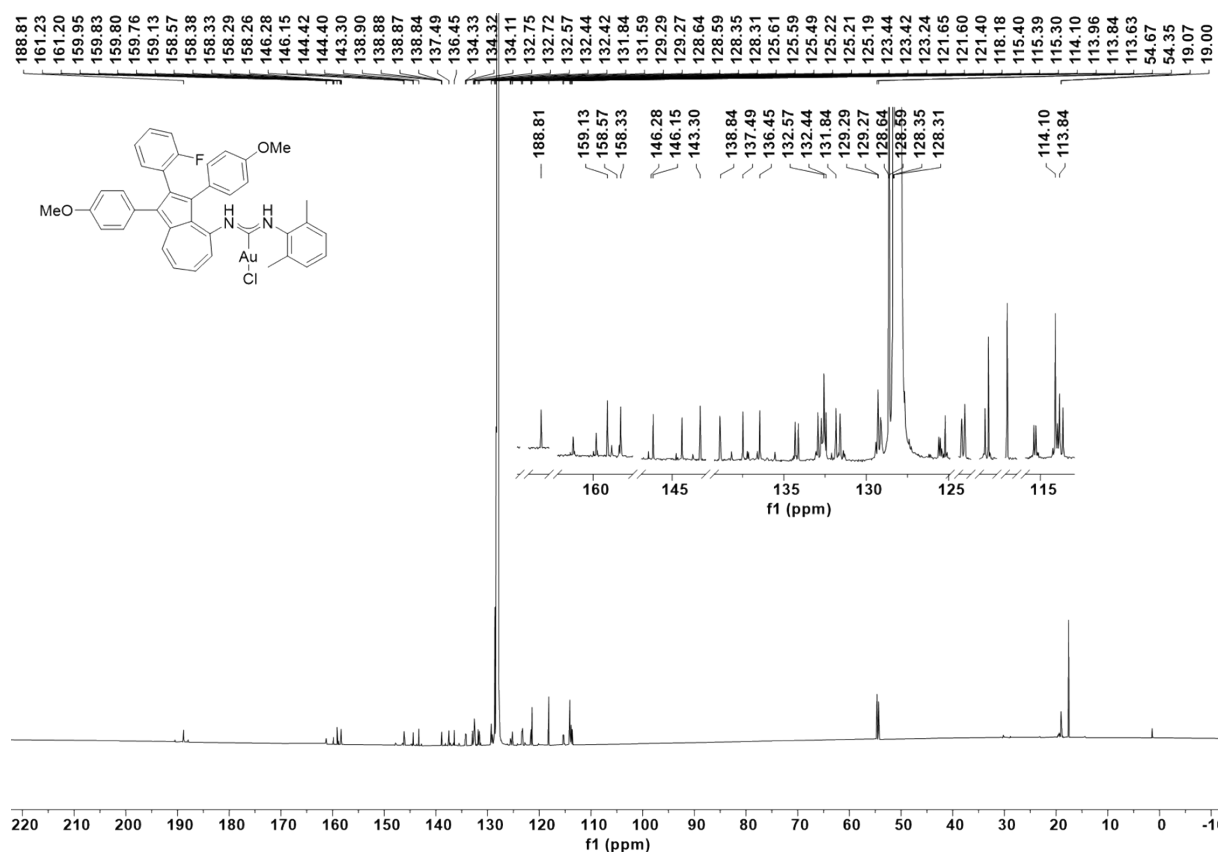


Figure S39. $^{13}\text{C}\{^{19}\text{F},^1\text{H}\}$ NMR Spectrum (176 MHz, C₆D₆, 295 K) of **14ad**.

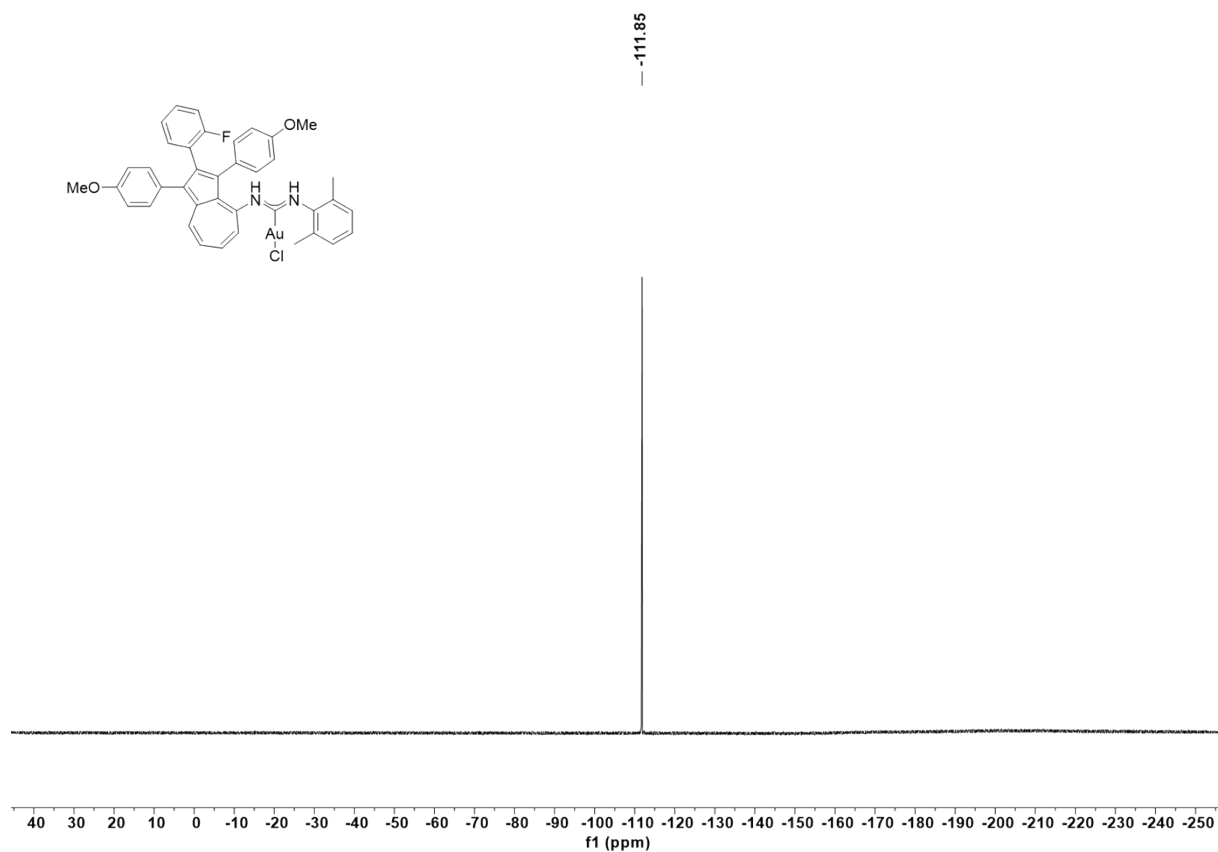


Figure S40. $^{19}\text{F}\{^1\text{H}\}$ NMR Spectrum (283 MHz, C₆D₆, 295 K) of **14ad**.

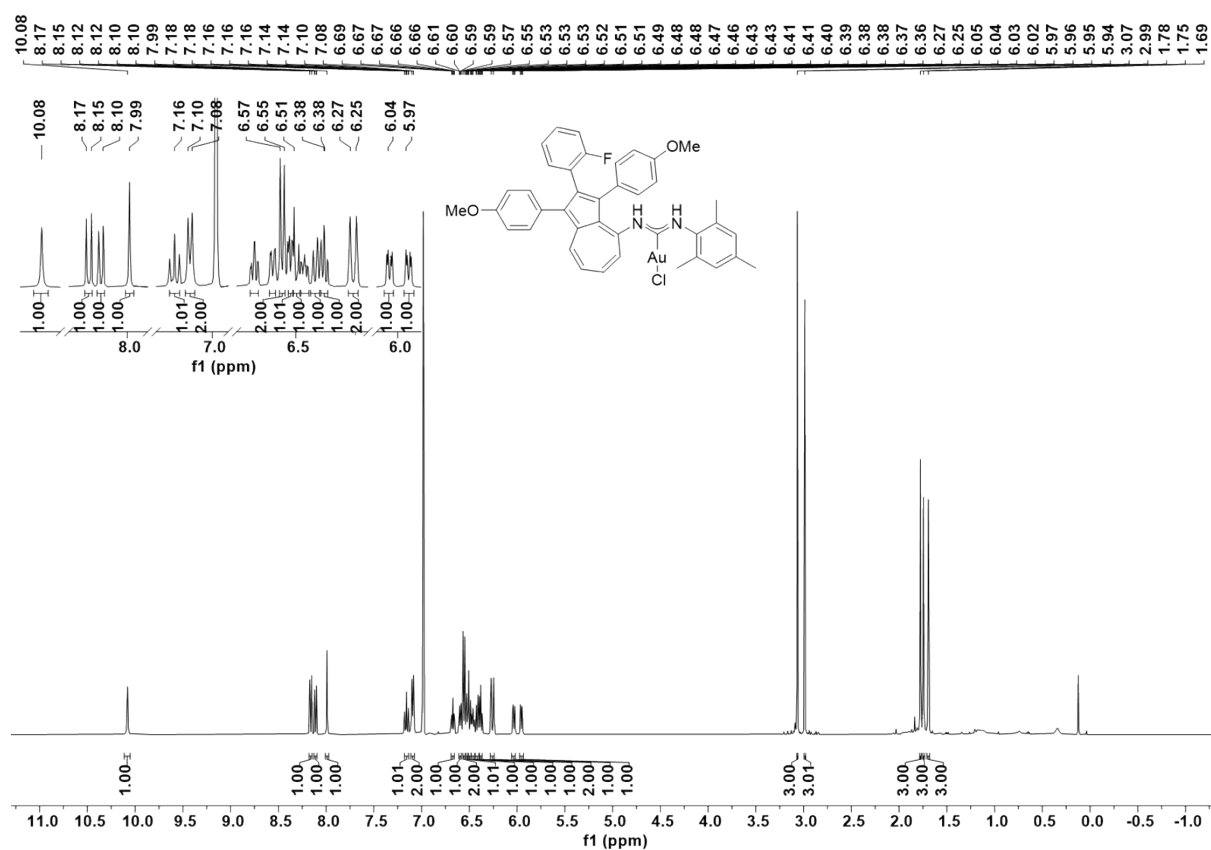


Figure S41. ¹H{¹⁹F} NMR Spectrum (500 MHz, C₆D₆, 295 K) of 14ae.

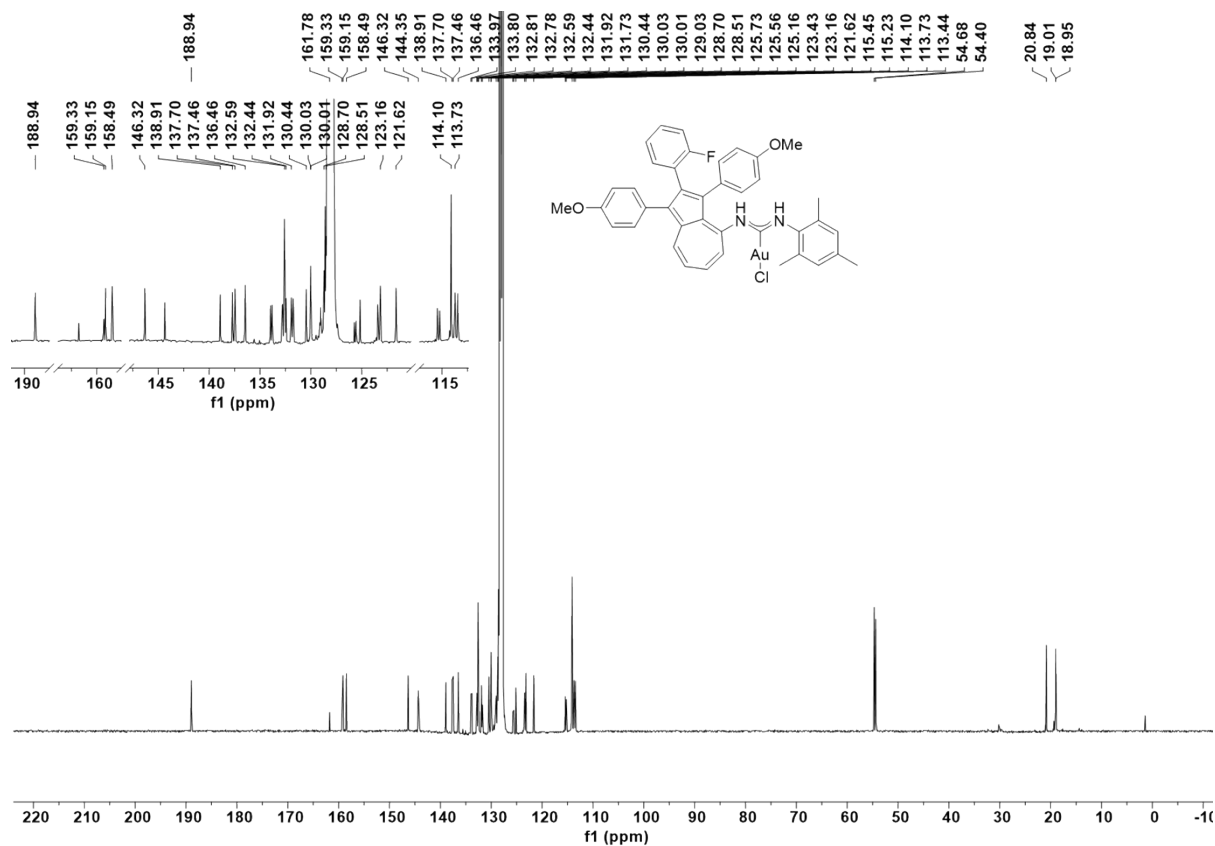


Figure S42. ¹³C{¹⁹F, ¹H} NMR Spectrum (101 MHz, C₆D₆, 295 K) of 14ae.

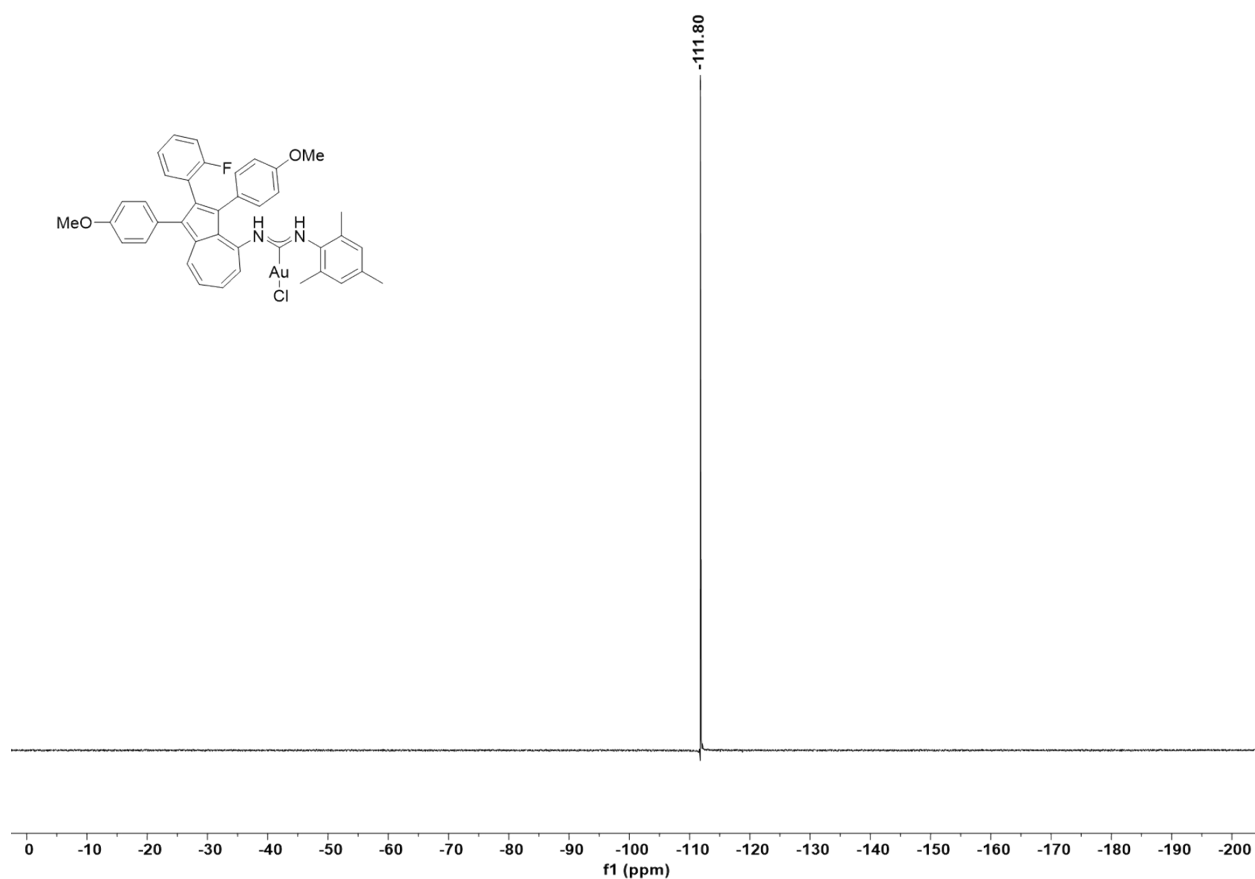


Figure S43. $^{19}\text{F}\{^1\text{H}\}$ NMR Spectrum (471 MHz, C_6D_6 , 295 K) of **14ae**.

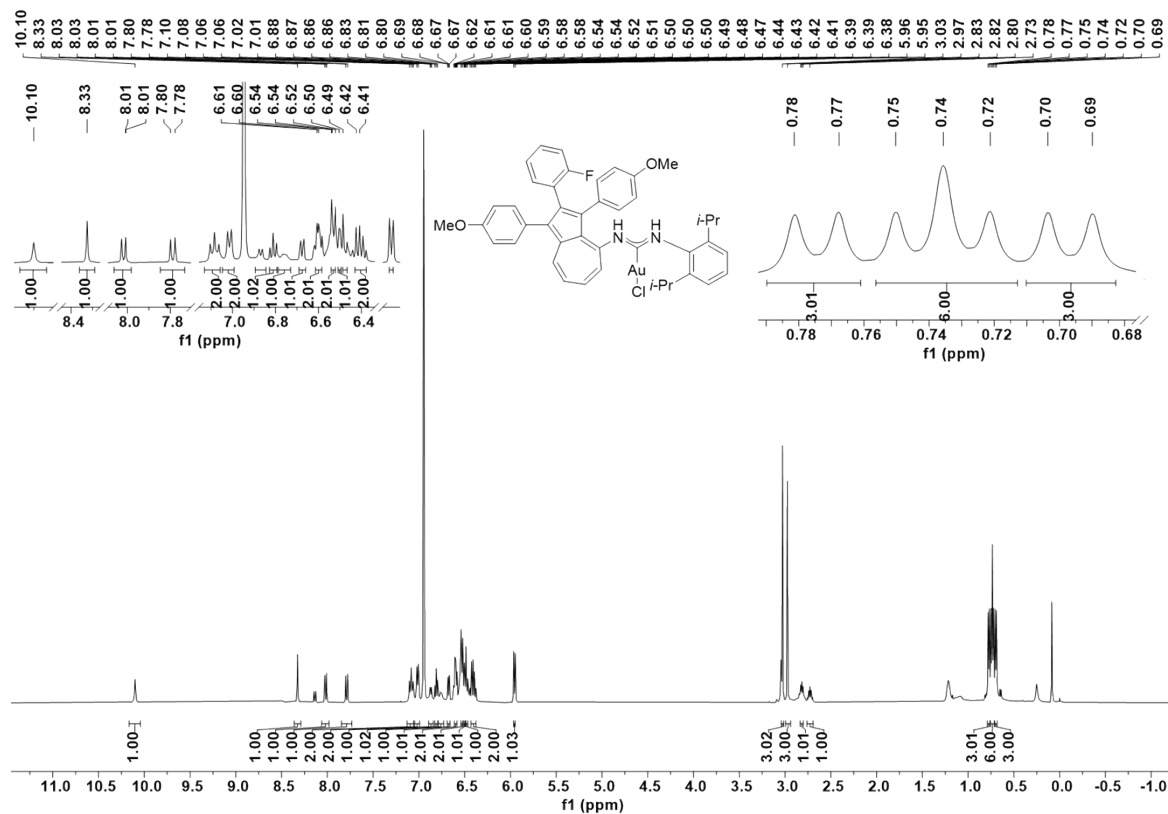


Figure S44. $^1\text{H}\{^{19}\text{F}\}$ NMR Spectrum (500 MHz, C_6D_6 , 295 K) of **14af**.

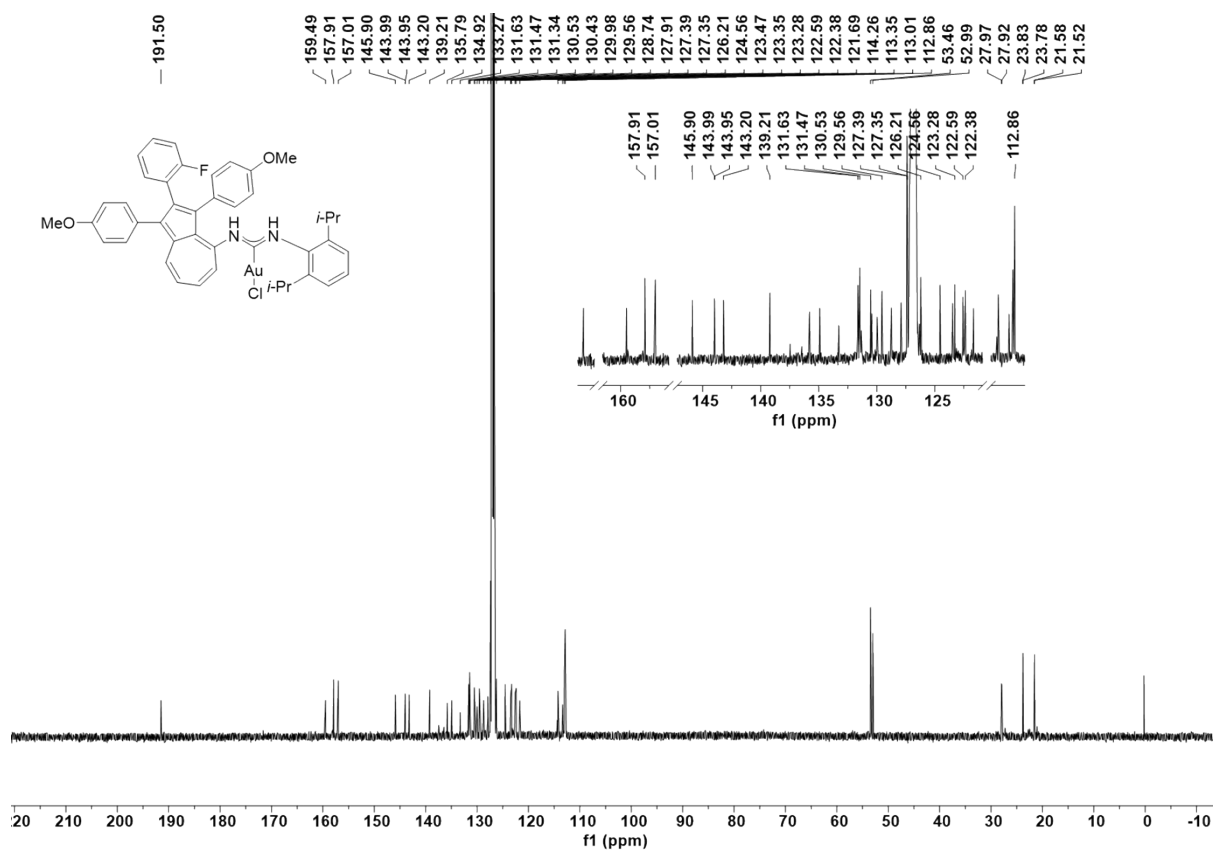


Figure S45. $^{13}\text{C}\{^{19}\text{F}, ^1\text{H}\}$ NMR Spectrum (126 MHz, C_6D_6 , 295 K) of **14af**.

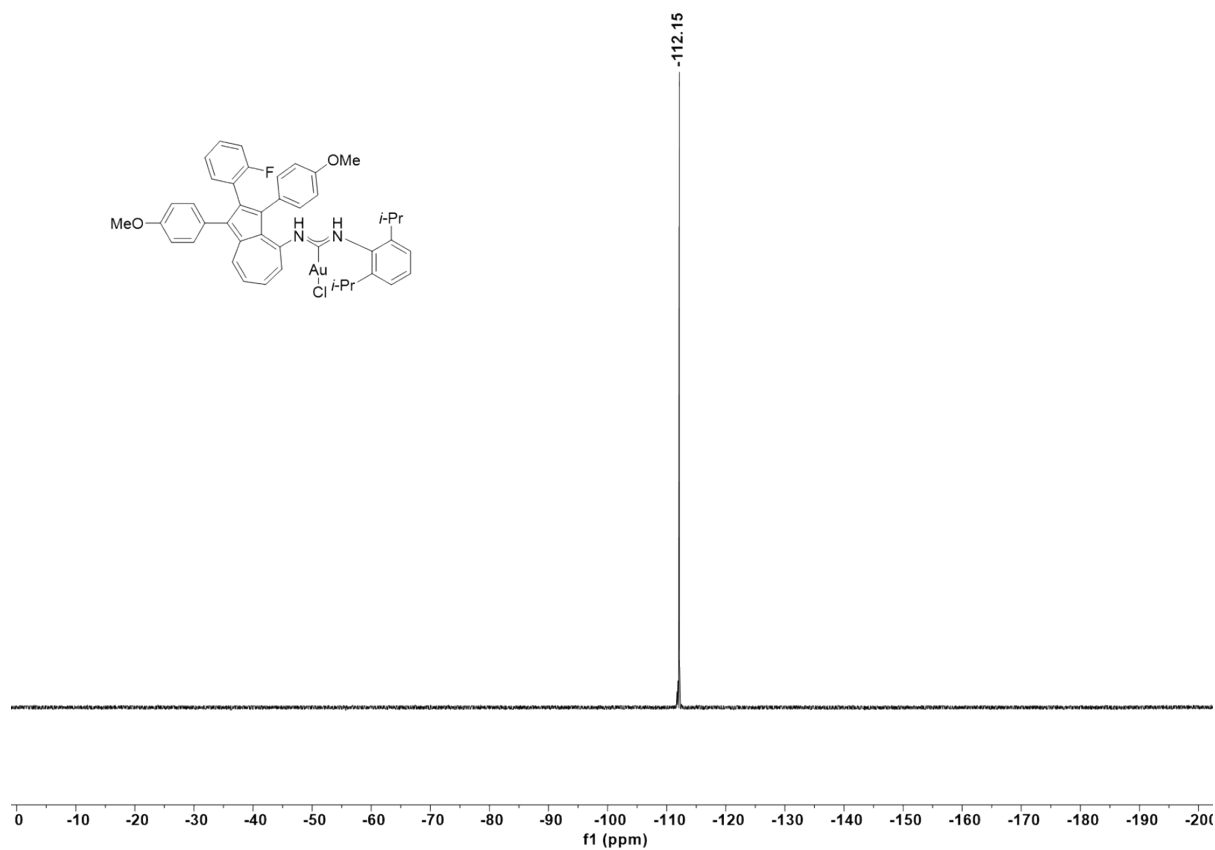


Figure S46. $^{19}\text{F}\{^1\text{H}\}$ NMR Spectrum (471 MHz, C_6D_6 , 295 K) of **14af**.

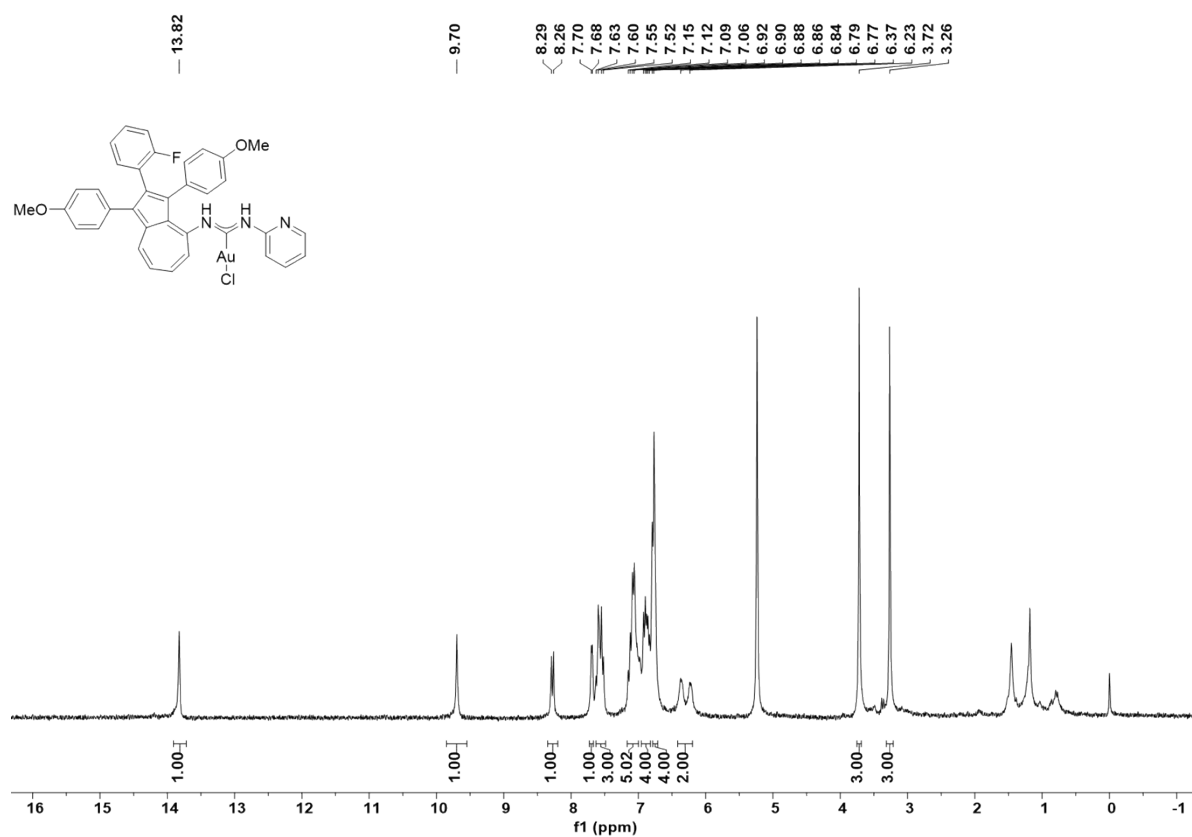


Figure S47. $^1\text{H}\{^{19}\text{F}\}$ NMR Spectrum (301 MHz, CD_2Cl_2 , 295 K) of **14ag**.

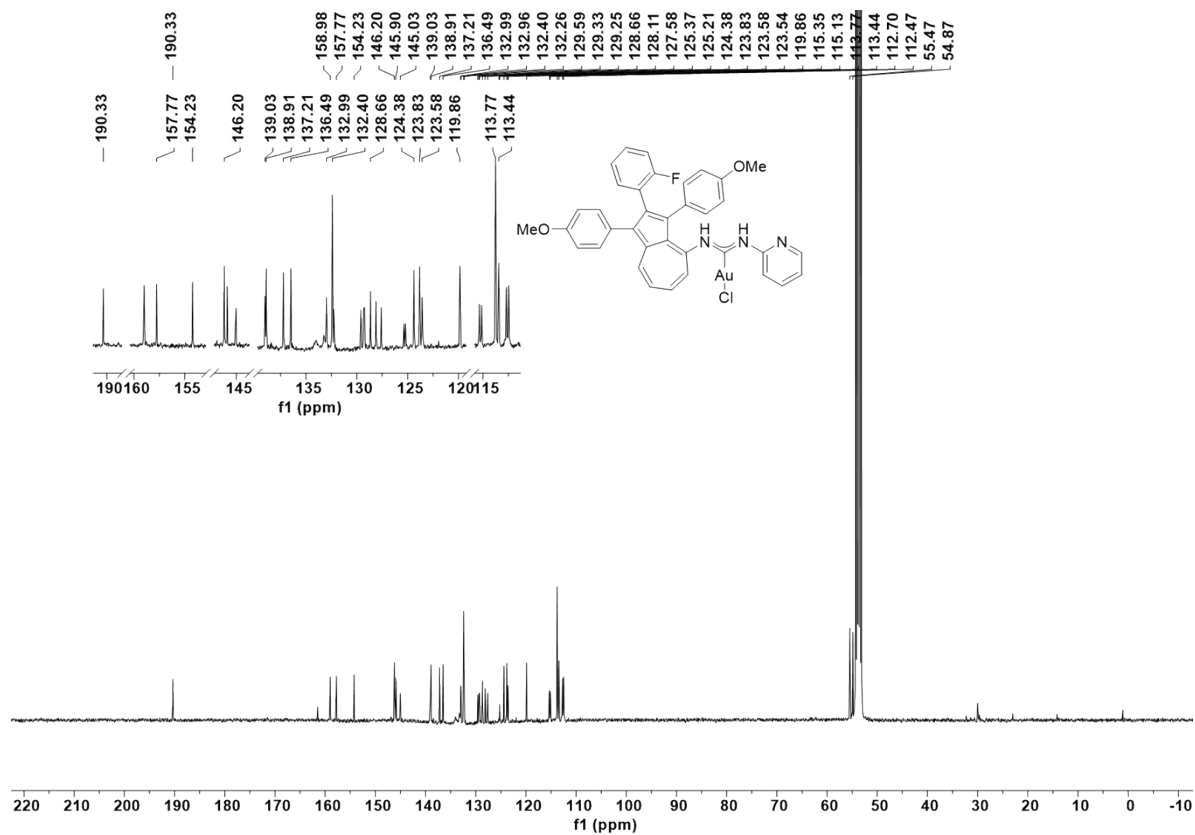


Figure S48. $^{13}\text{C}\{^{19}\text{F}, ^1\text{H}\}$ NMR Spectrum (101 MHz, CD_2Cl_2 , 295 K) of **14ag**.

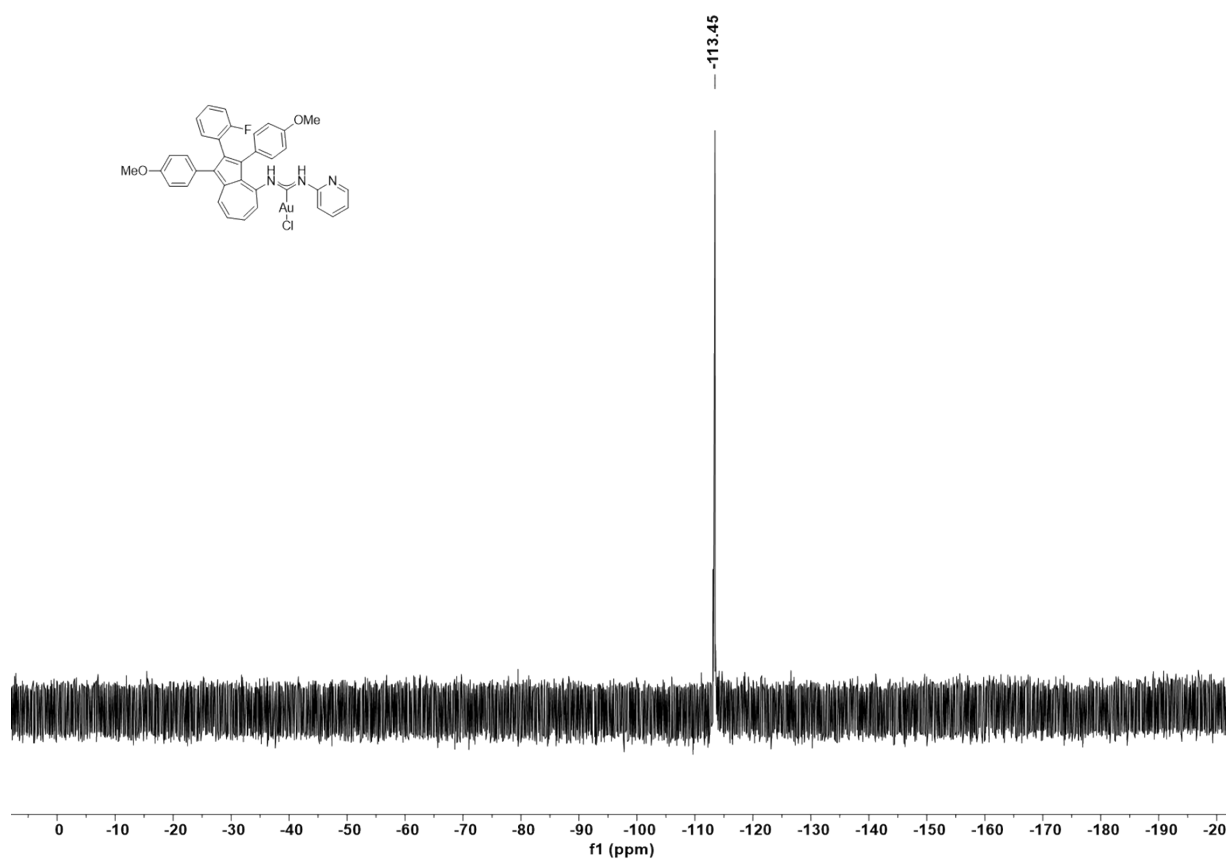


Figure S49. $^{19}\text{F}\{^1\text{H}\}$ NMR Spectrum (471 MHz, CD_2Cl_2 , 295 K) of **14ag**.

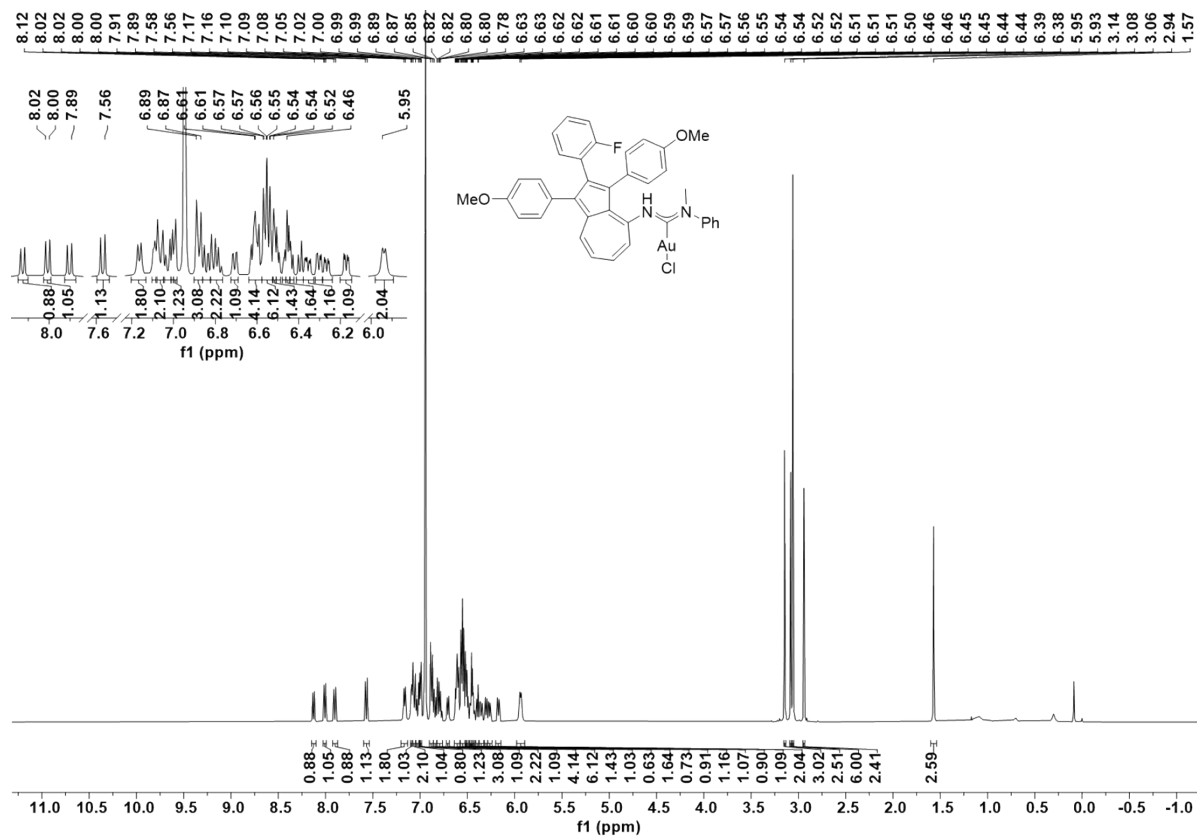


Figure S50. $^1\text{H}\{^{19}\text{F}\}$ NMR Spectrum (500 MHz, C_6D_6 , 295 K) of **14ah**.

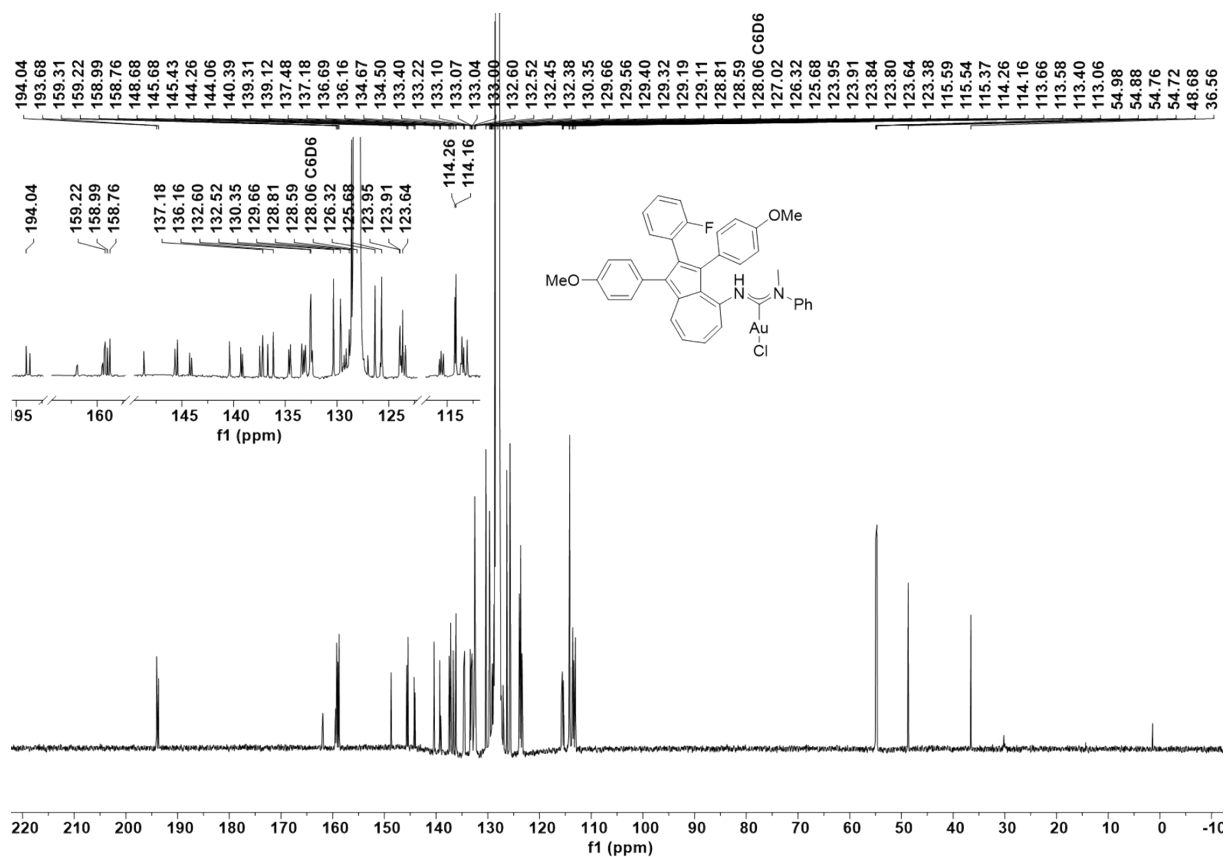


Figure S51. $^{13}\text{C}\{^{19}\text{F}, ^1\text{H}\}$ NMR Spectrum (101 MHz, C_6D_6 , 295 K) of **14ah**.

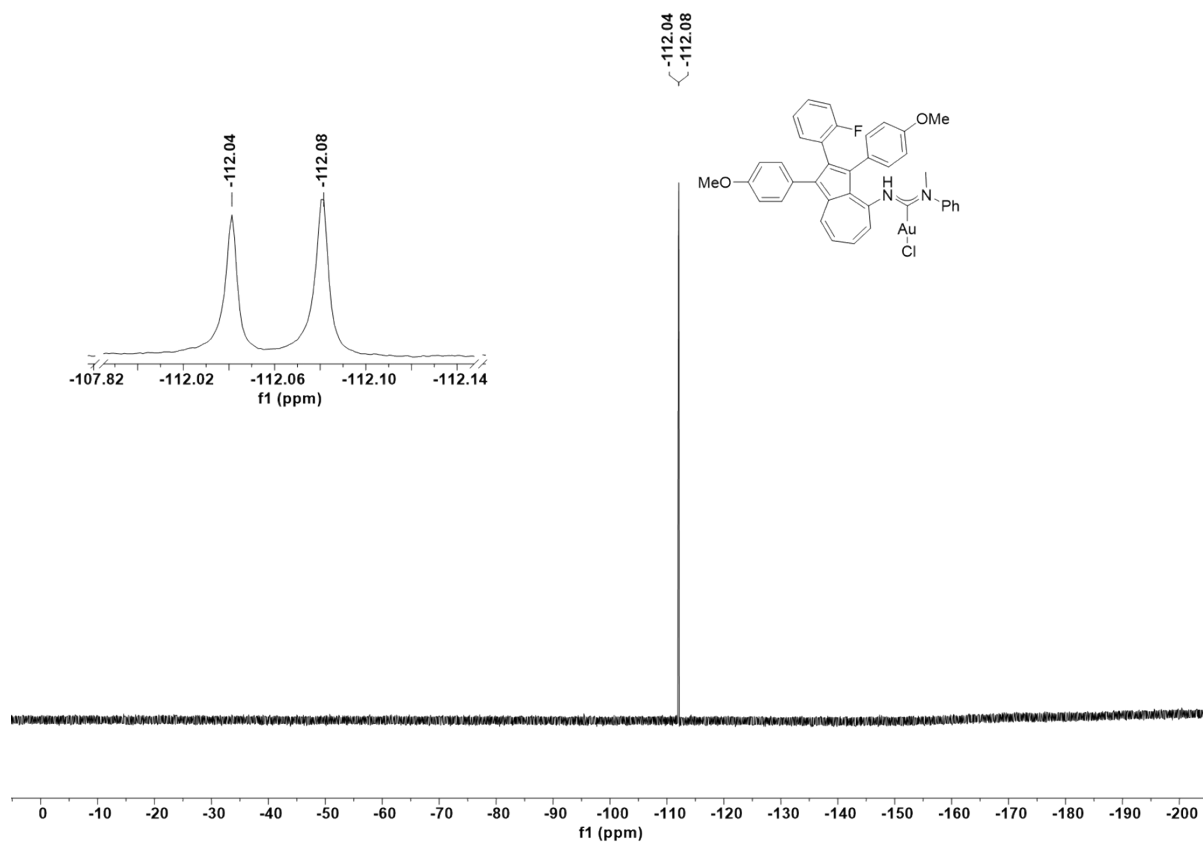


Figure S52. $^{19}\text{F}\{^1\text{H}\}$ NMR Spectrum (283 MHz, C_6D_6 , 295 K) of **14ah**.

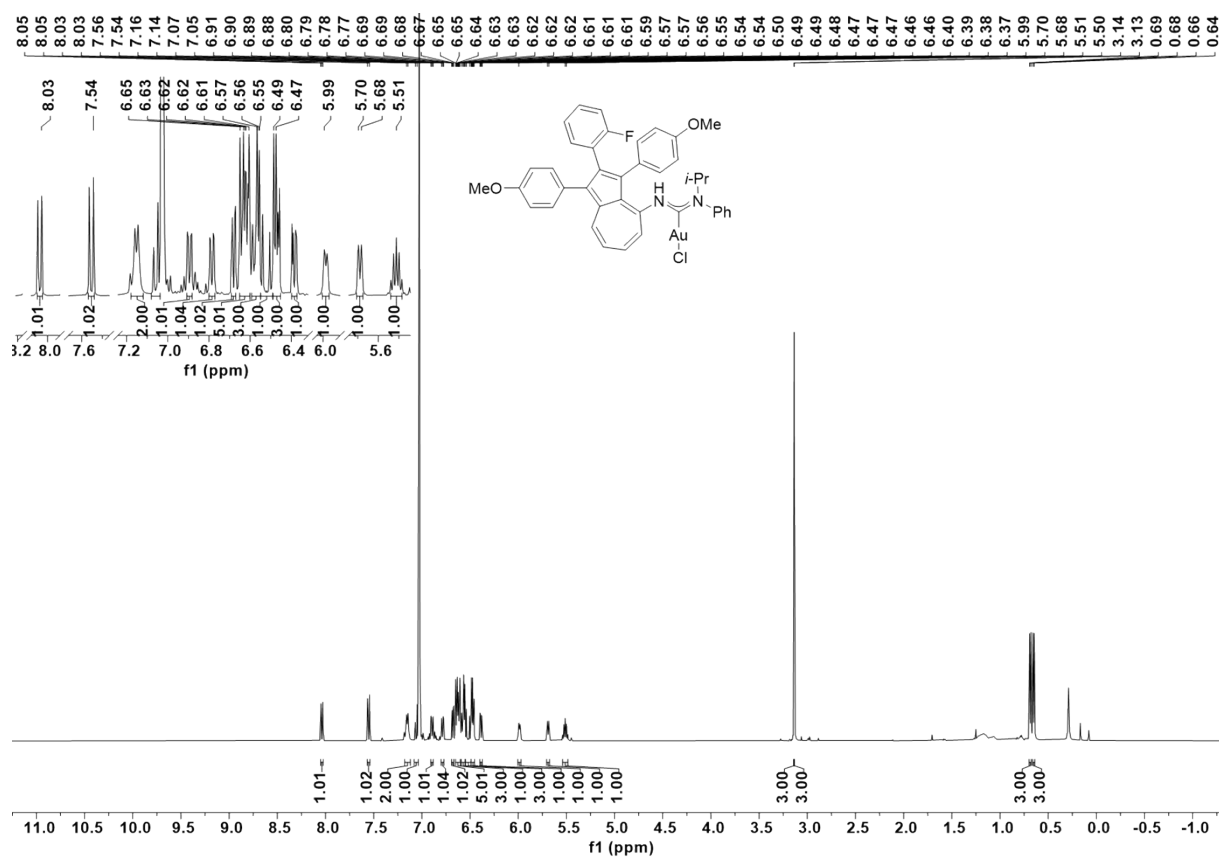


Figure S53. ¹H{¹⁹F} NMR Spectrum (500 MHz, C₆D₆, 295 K) of 14ai.

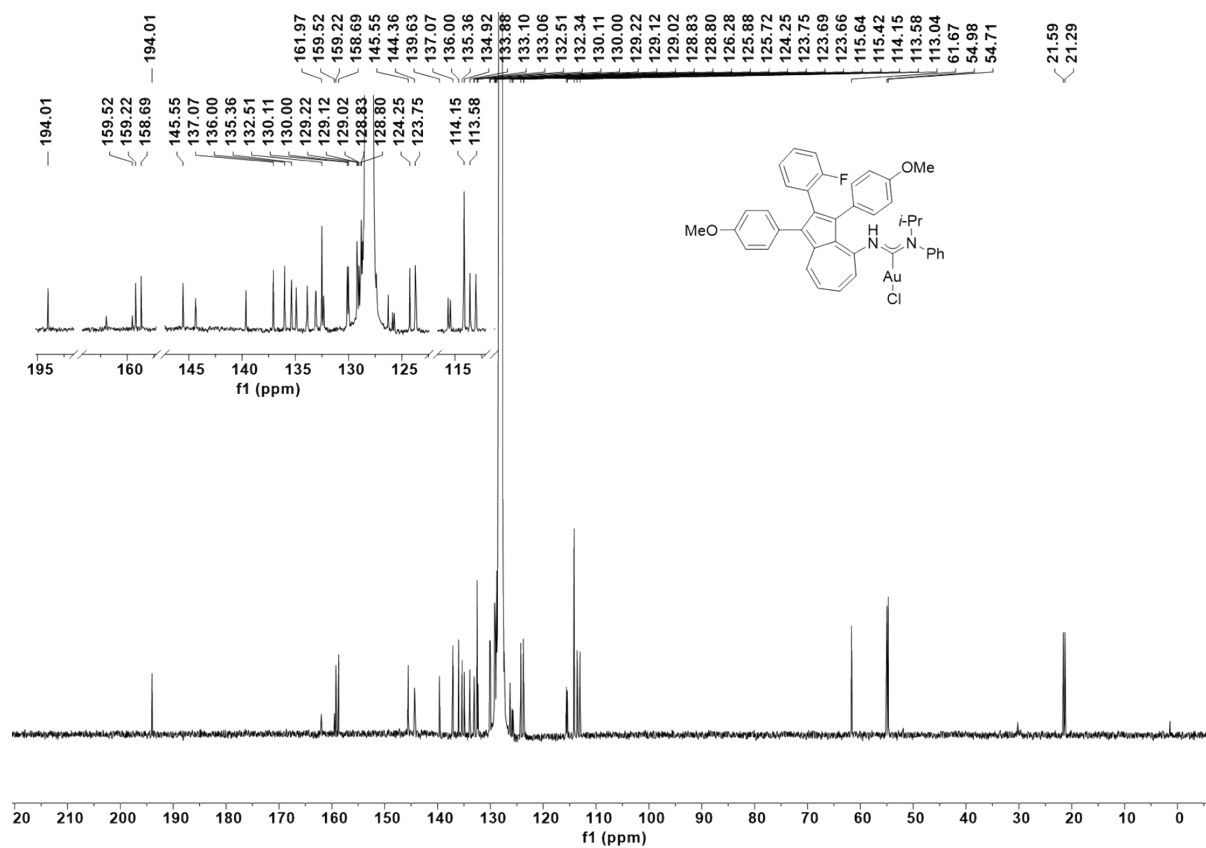


Figure S54. ¹³C{¹⁹F, ¹H} NMR Spectrum (101 MHz, C₆D₆, 295 K) of 14ai.

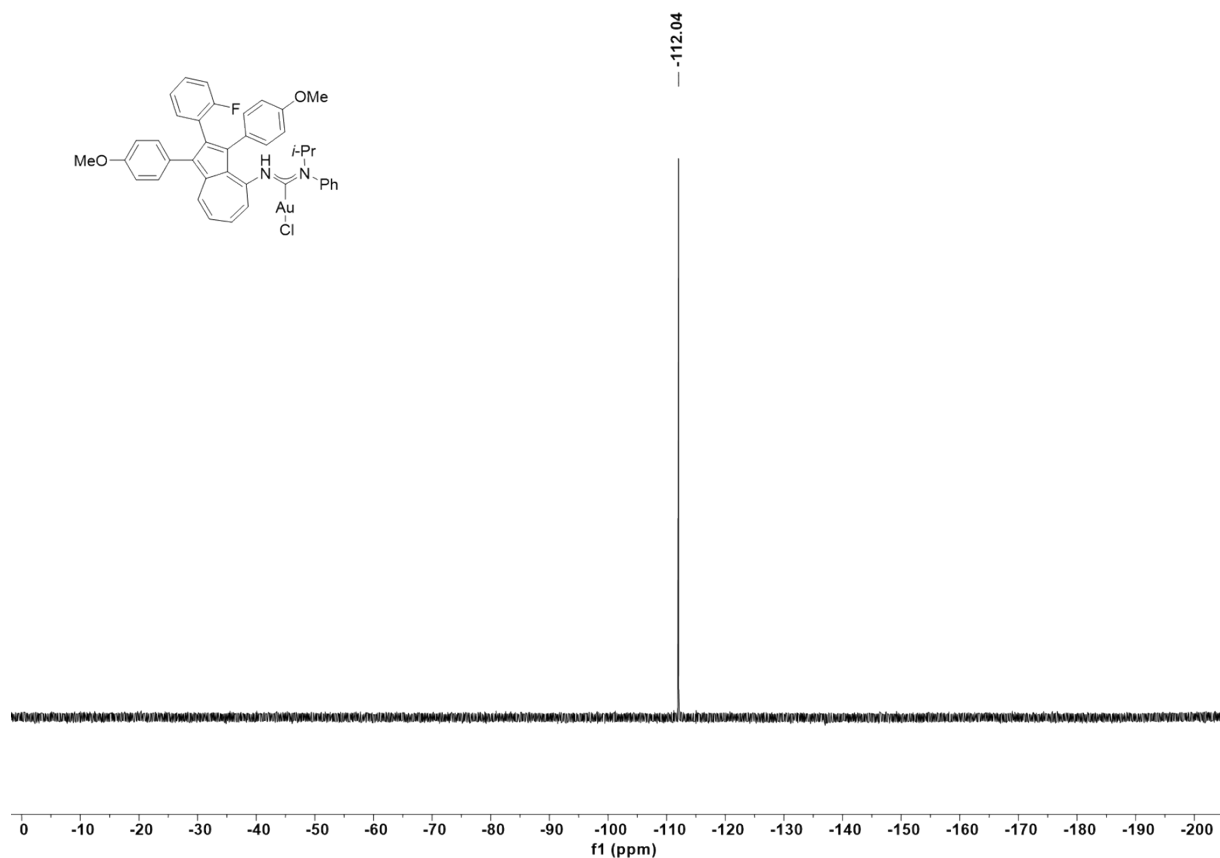


Figure S55. $^{19}\text{F}\{^1\text{H}\}$ NMR Spectrum (471 MHz, C_6D_6 , 295 K) of **14ai**.

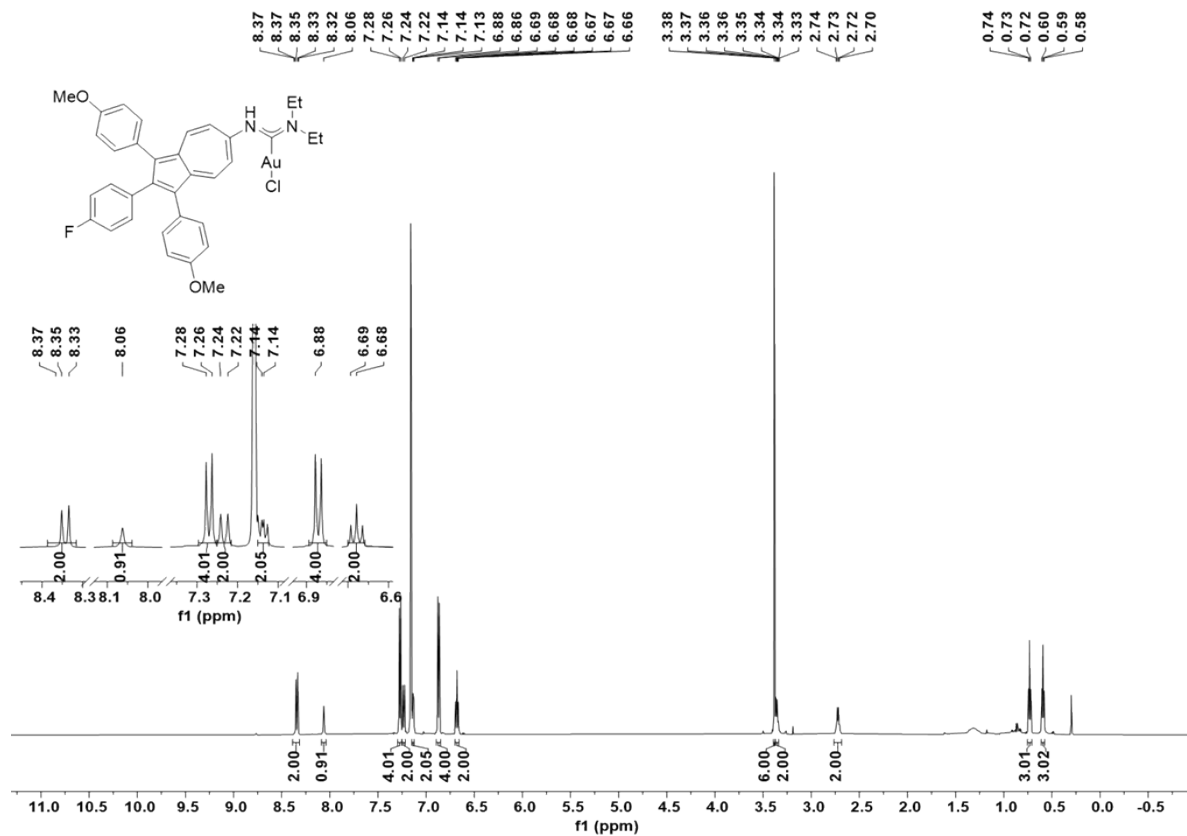


Figure S56. $^1\text{H}\{^{19}\text{F}\}$ NMR Spectrum (600 MHz, C_6D_6 , 295 K) of **14ba**.

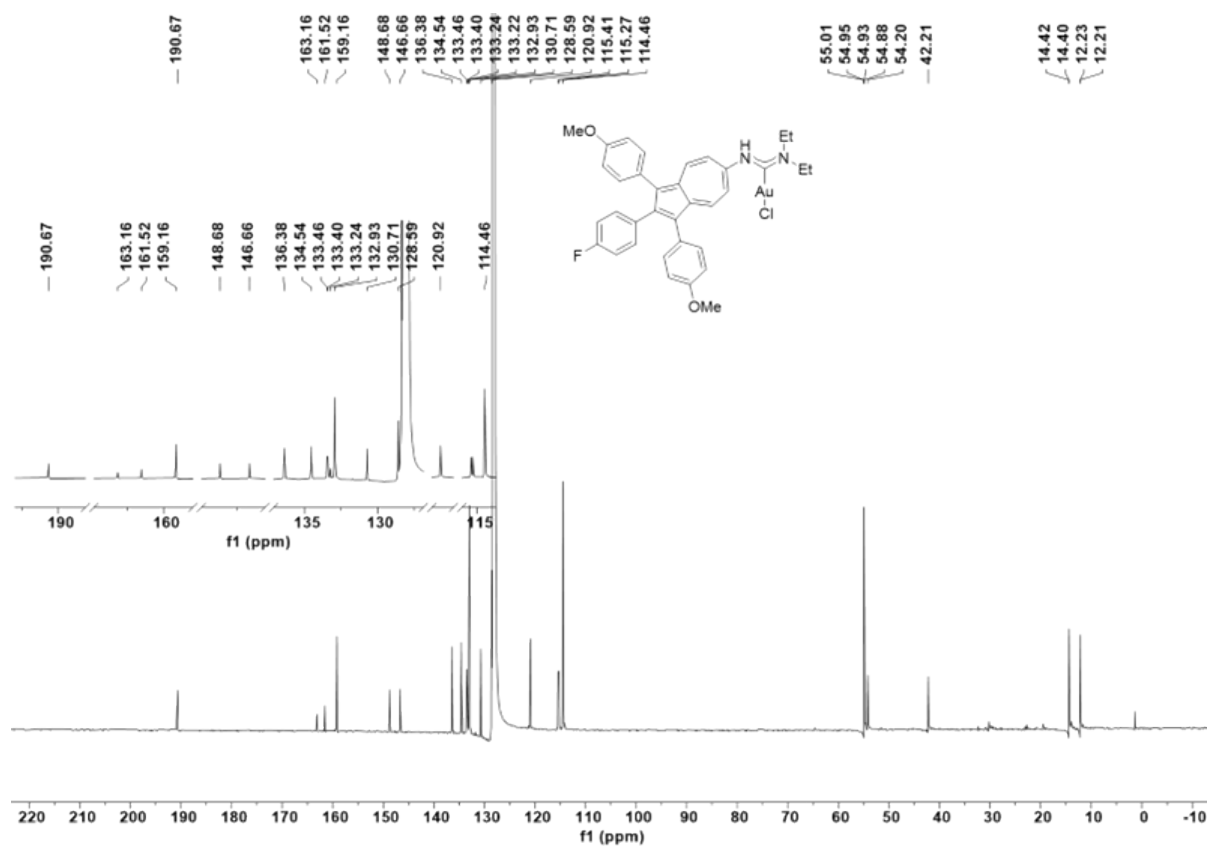


Figure S57. $^{13}\text{C}\{^{19}\text{F}, ^1\text{H}\}$ NMR Spectrum (151 MHz, C_6D_6 , 295 K) of 14ba.

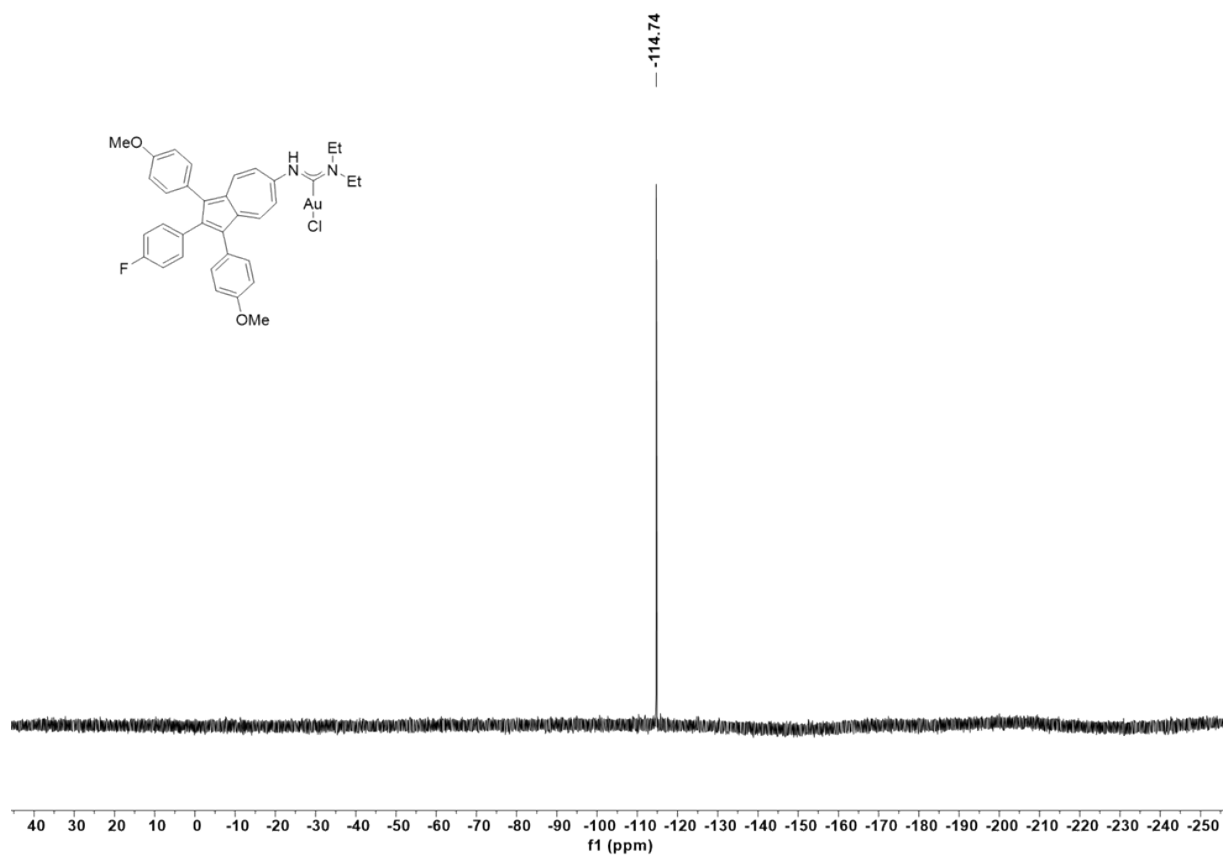


Figure S58. $^{19}\text{F}\{^1\text{H}\}$ NMR Spectrum (283 MHz, C_6D_6 , 295 K) of 14ba.

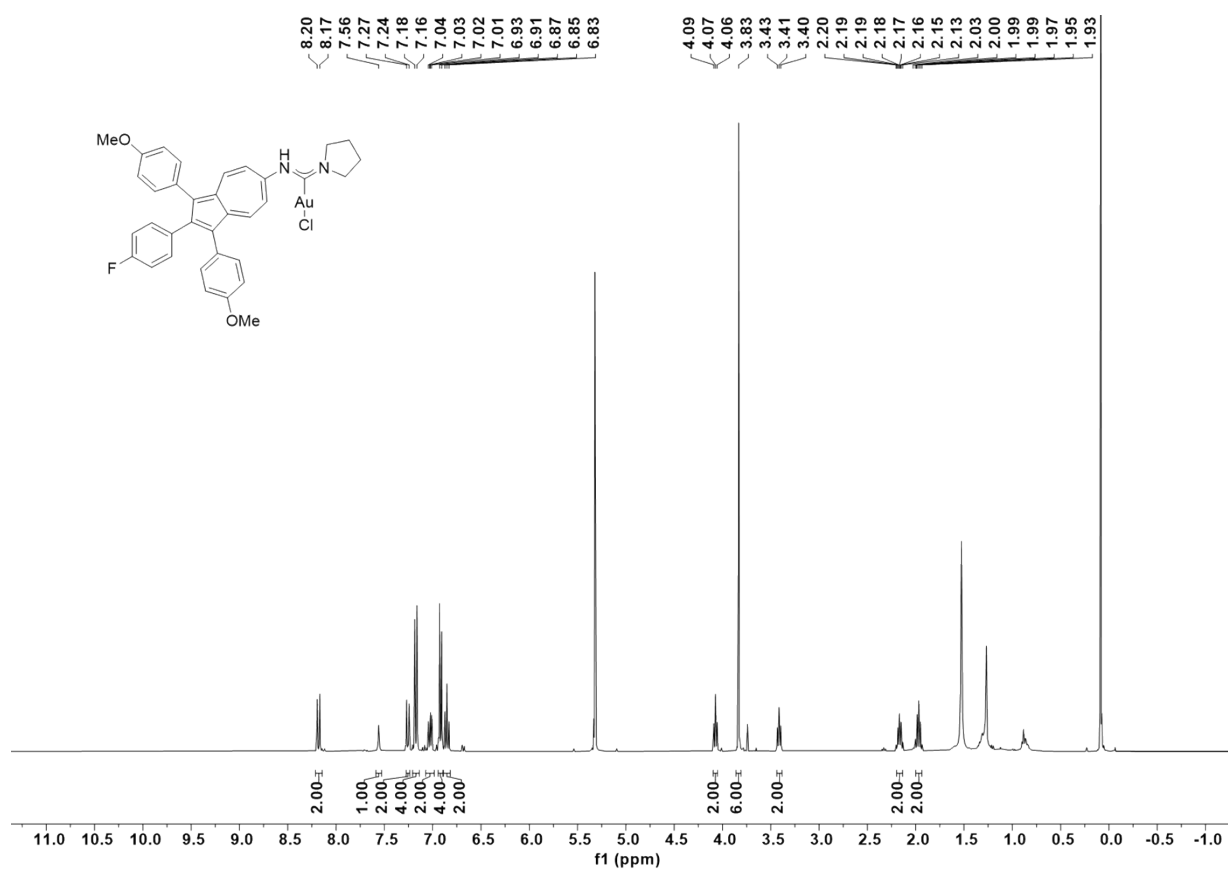


Figure S59. ¹H{¹⁹F} NMR Spectrum (400 MHz, CD₂Cl₂, 295 K) of **14bb**.

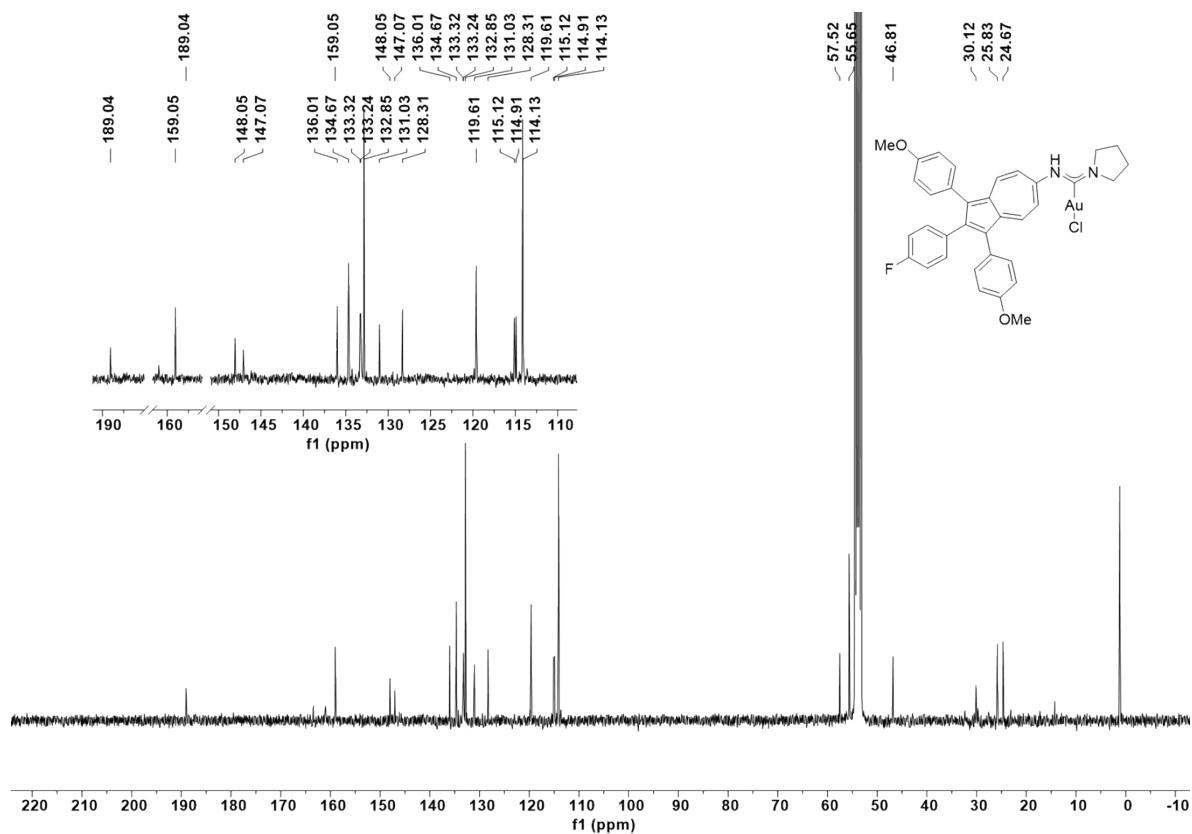


Figure S60. ¹³C{¹⁹F, ¹H} NMR Spectrum (101 MHz, CD₂Cl₂, 295 K) of **14bb**.

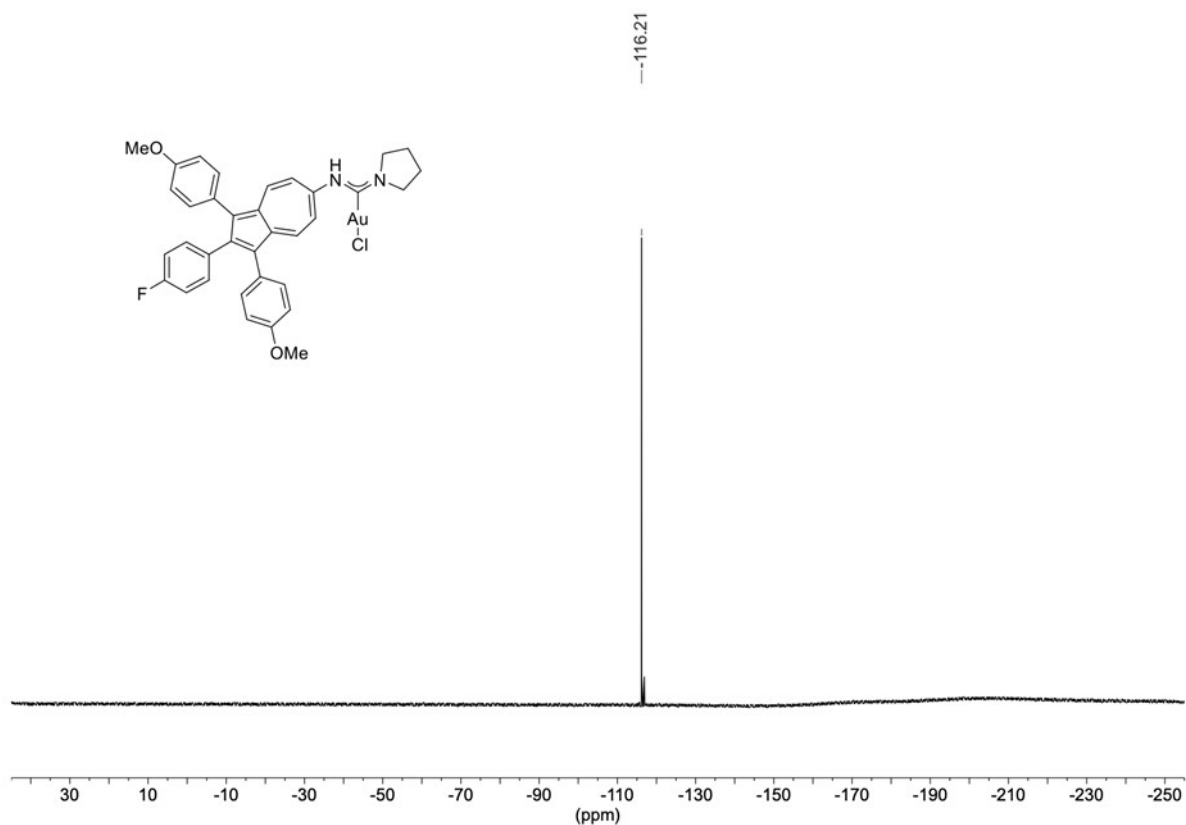


Figure S61. $^{19}\text{F}\{^1\text{H}\}$ NMR Spectrum (283 MHz, CD_2Cl_2 , 298 K) of **14bb**.

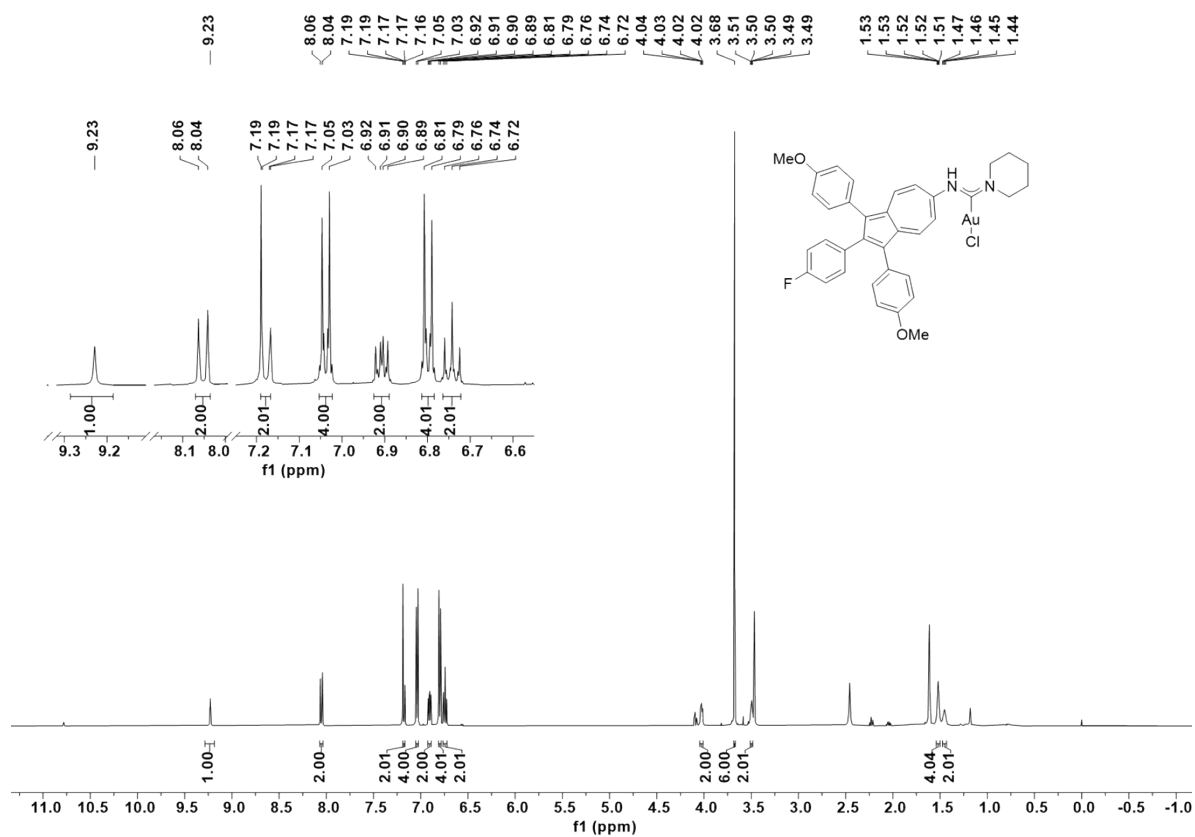


Figure S62. $^1\text{H}\{^{19}\text{F}\}$ NMR Spectrum (500 MHz, THF-d_8 , 295 K) of **14bc**.

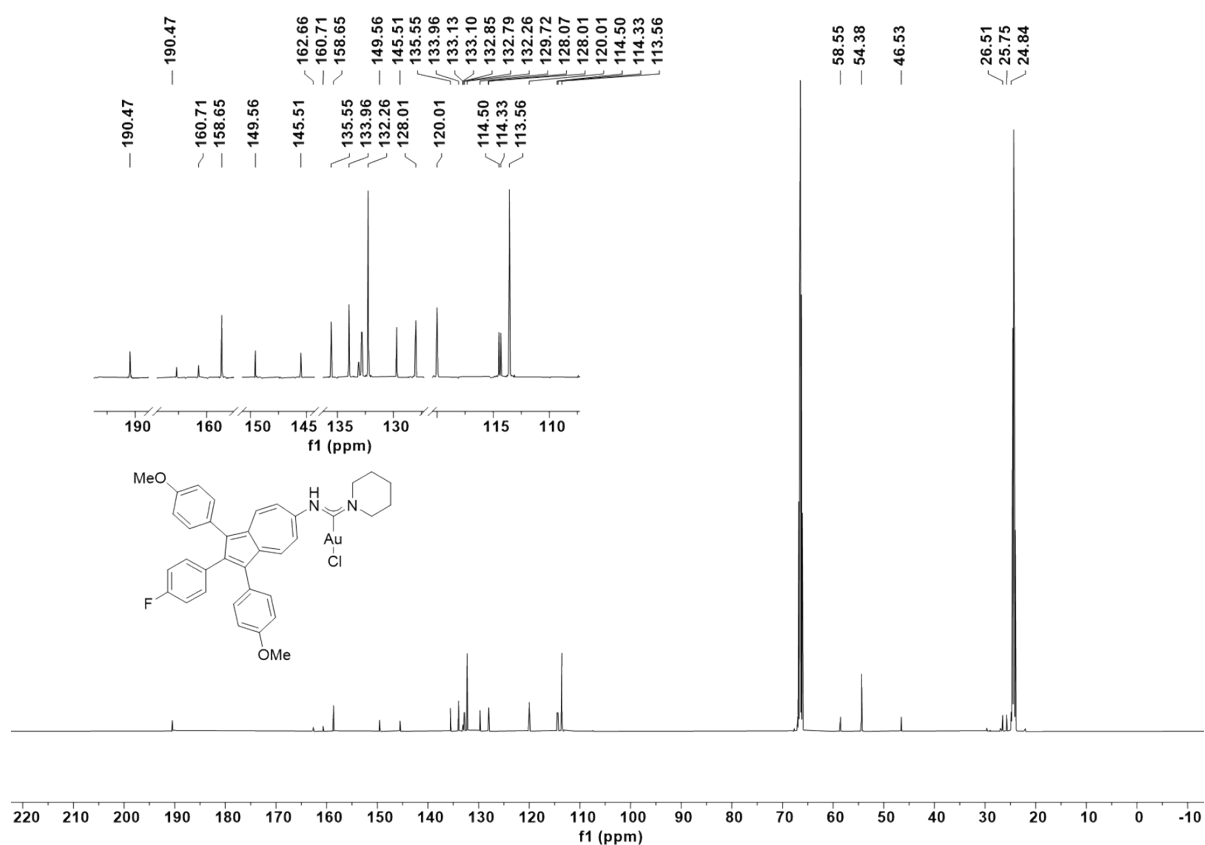


Figure S63. $^{13}\text{C}\{^{19}\text{F},^1\text{H}\}$ NMR Spectrum (126 MHz, THF- d_8 , 295 K) of **14bc**.

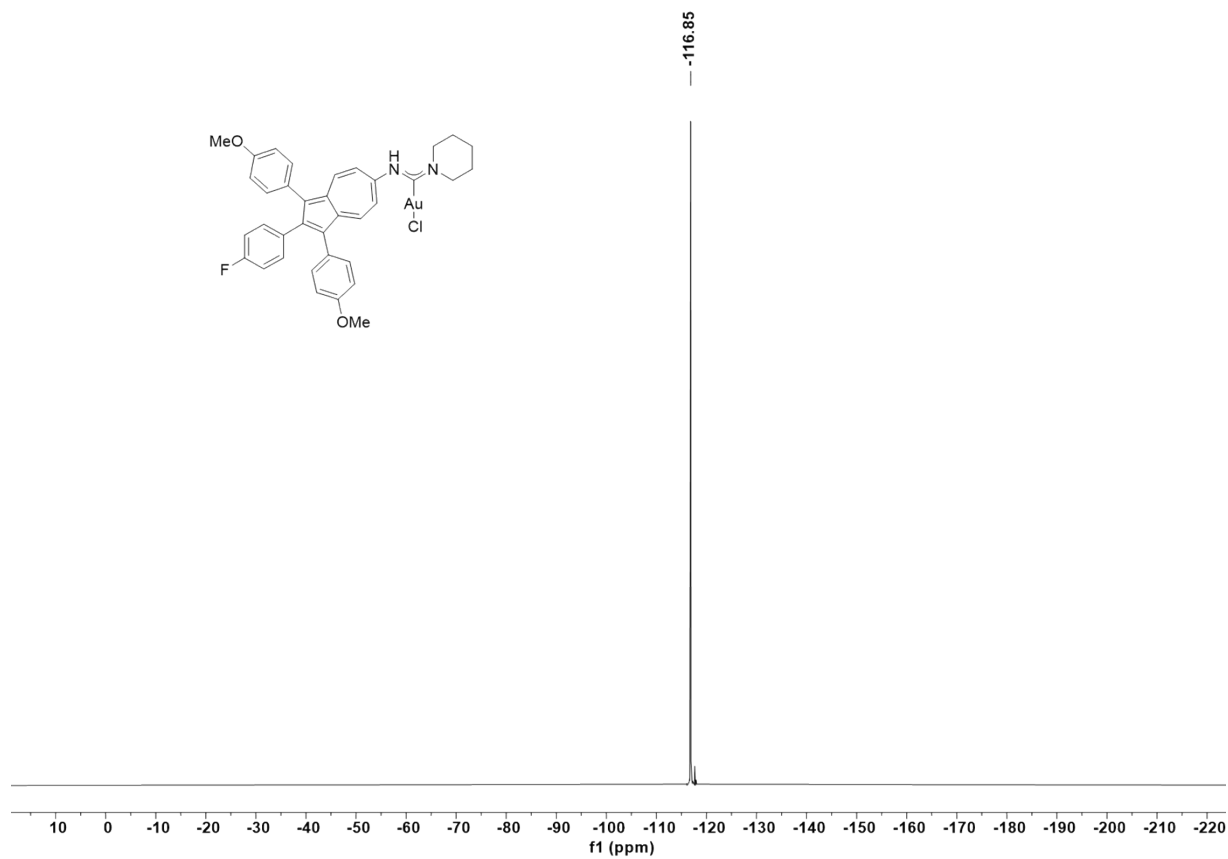


Figure S64. $^{19}\text{F}\{^1\text{H}\}$ NMR Spectrum (471 MHz, THF- d_8 , 295 K) of **14bc**.

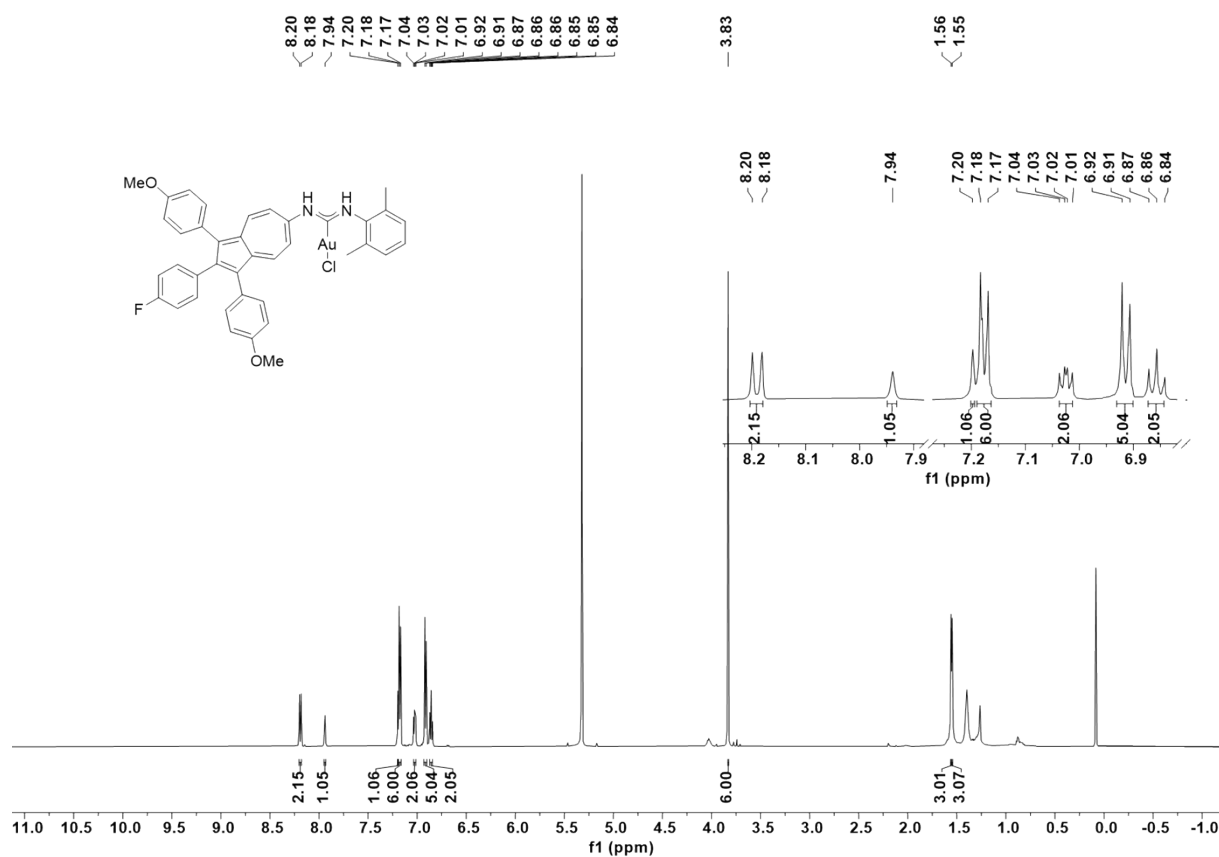


Figure S65. $^1\text{H}\{^{19}\text{F}\}$ NMR Spectrum (600 MHz, CD_2Cl_2 , 295 K) of **14bd**.

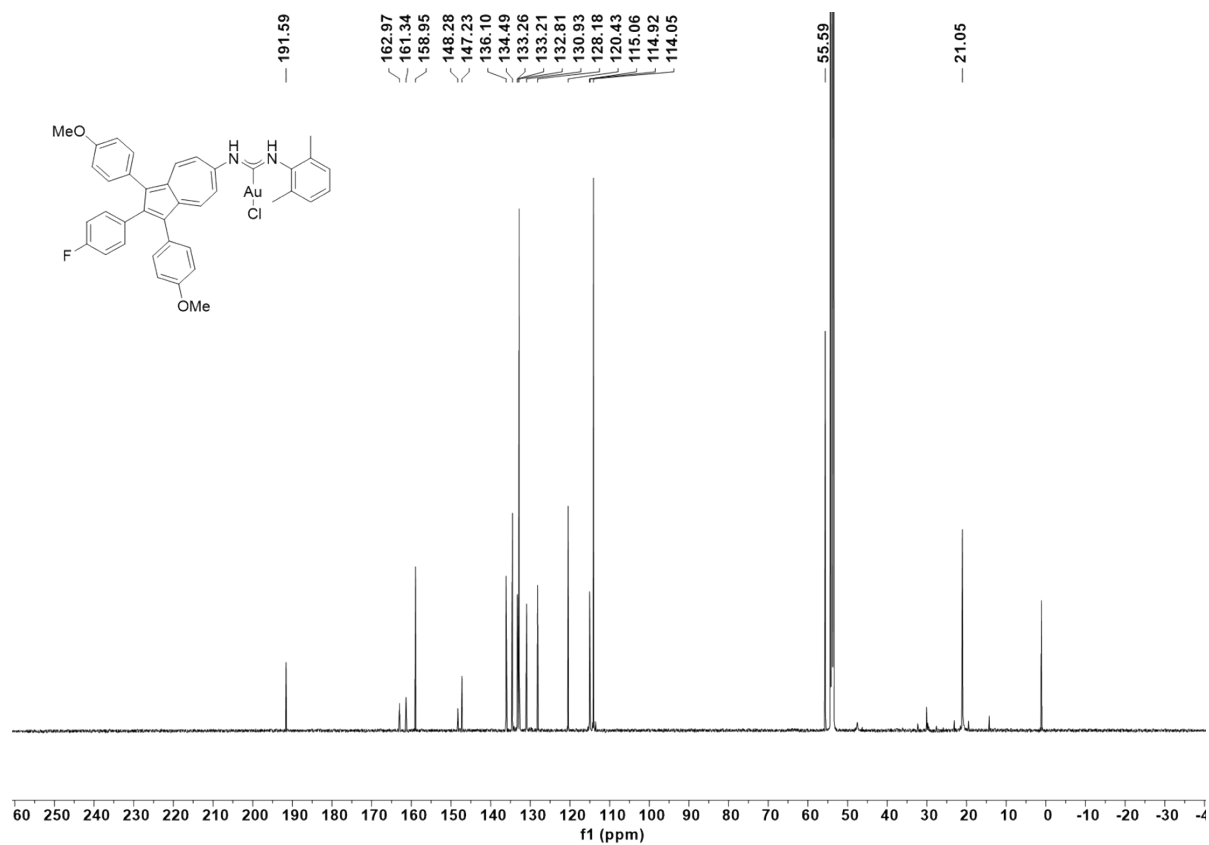


Figure S66. $^{13}\text{C}\{^{19}\text{F}, ^1\text{H}\}$ NMR Spectrum (151 MHz, CD_2Cl_2 , 295 K) of **14bd**.

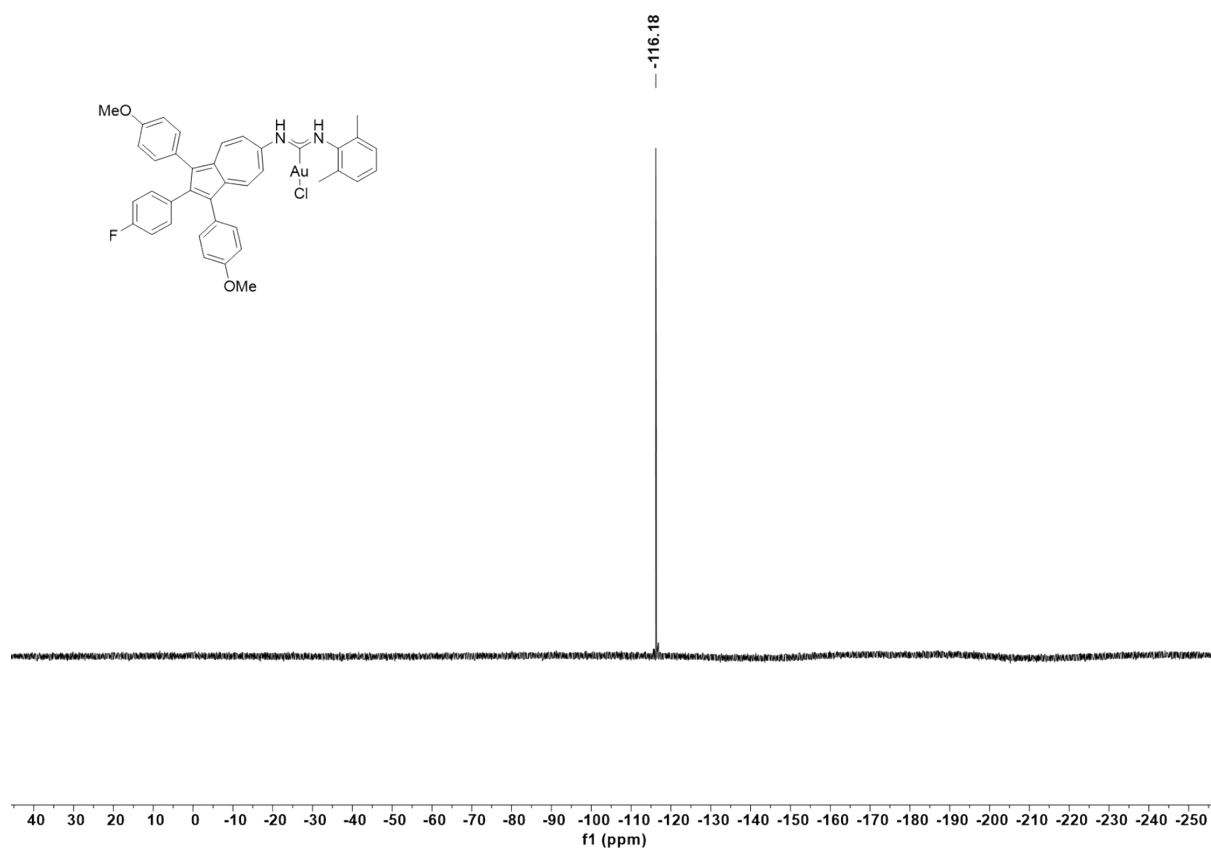


Figure S67. $^{19}\text{F}\{^1\text{H}\}$ NMR Spectrum (283 MHz, CD_2Cl_2 , 295 K) of **14bd**.

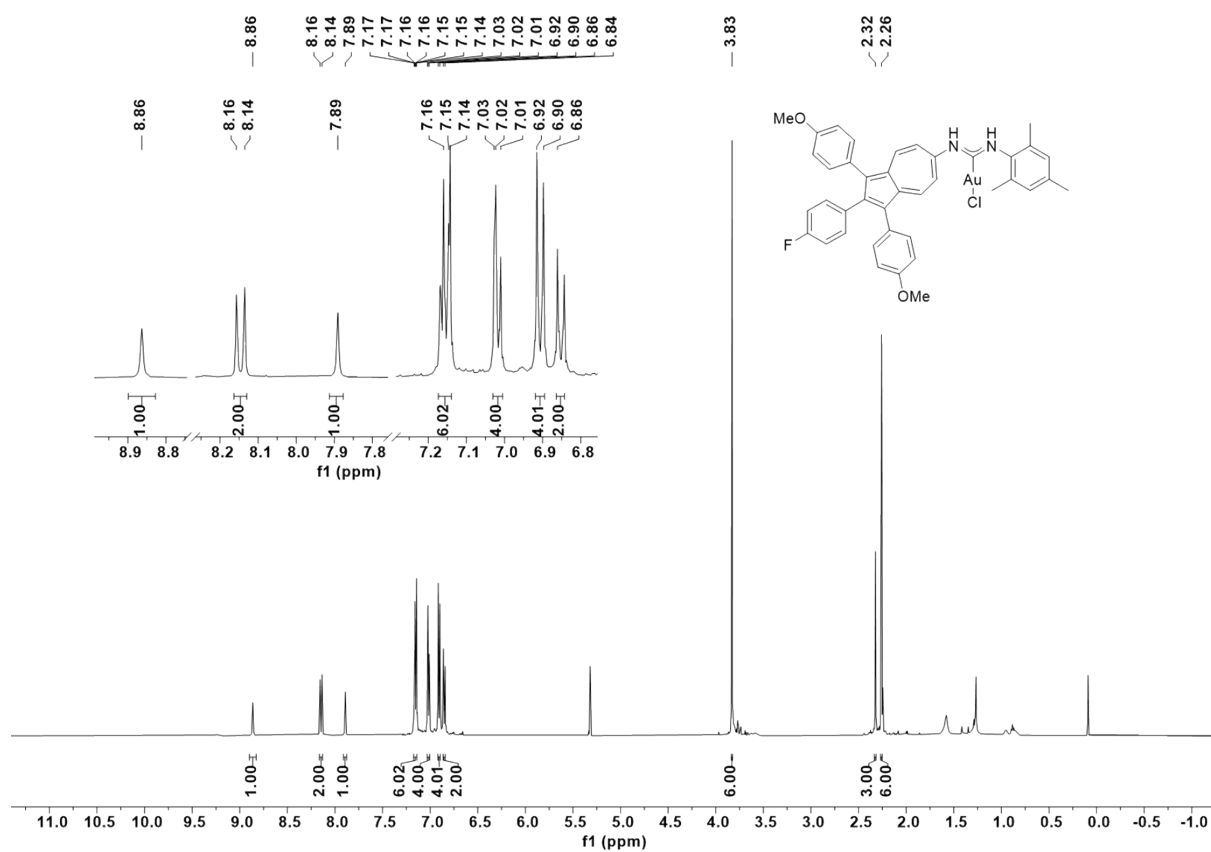


Figure S68. $^1\text{H}\{^{19}\text{F}\}$ NMR Spectrum (500 MHz, CD_2Cl_2 , 295 K) of **14be**.

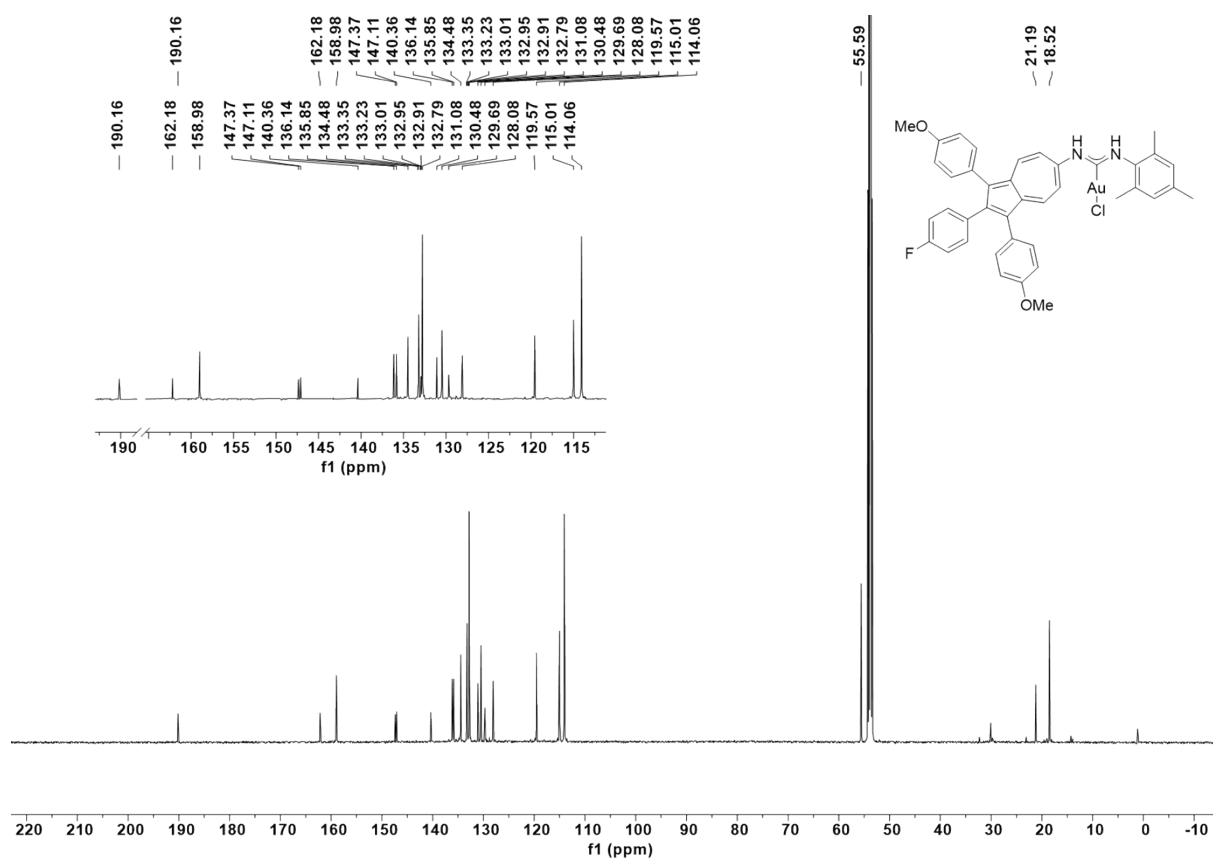


Figure S69. $^{13}\text{C}\{^{19}\text{F}, ^1\text{H}\}$ NMR Spectrum (126 MHz, CD_2Cl_2 , 295 K) of **14be**.

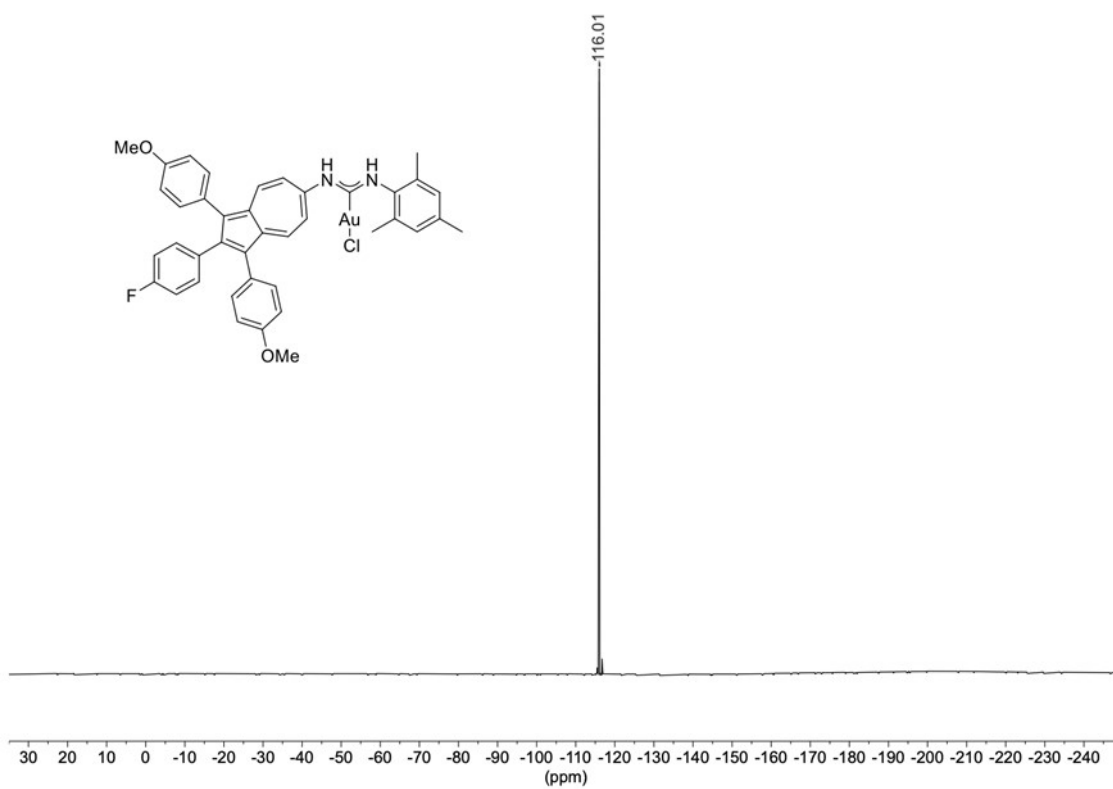


Figure S70. $^{19}\text{F}\{^1\text{H}\}$ NMR Spectrum (283 MHz, CD_2Cl_2 , 298 K) of **14be**.

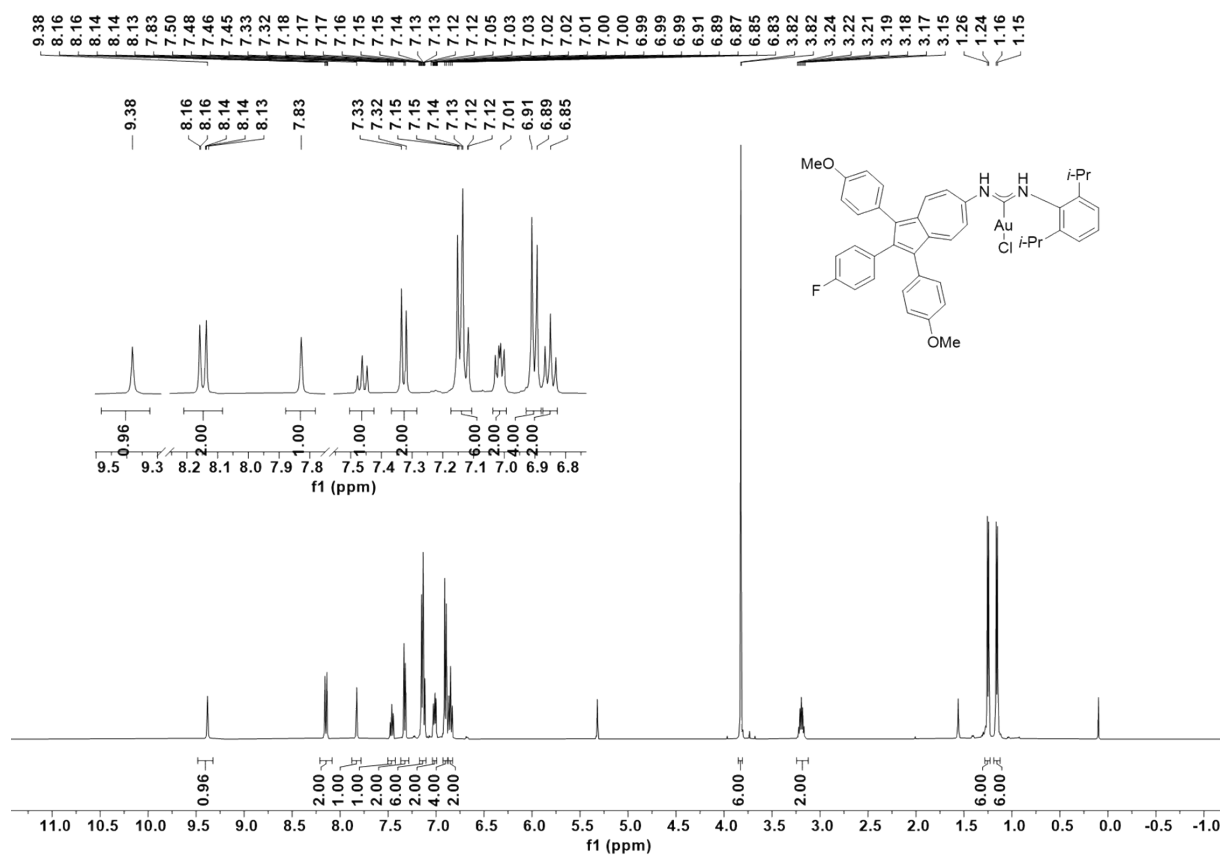


Figure S71. $^1\text{H}\{^{19}\text{F}\}$ NMR Spectrum (500 MHz, CD_2Cl_2 , 295 K) of **14bf**.

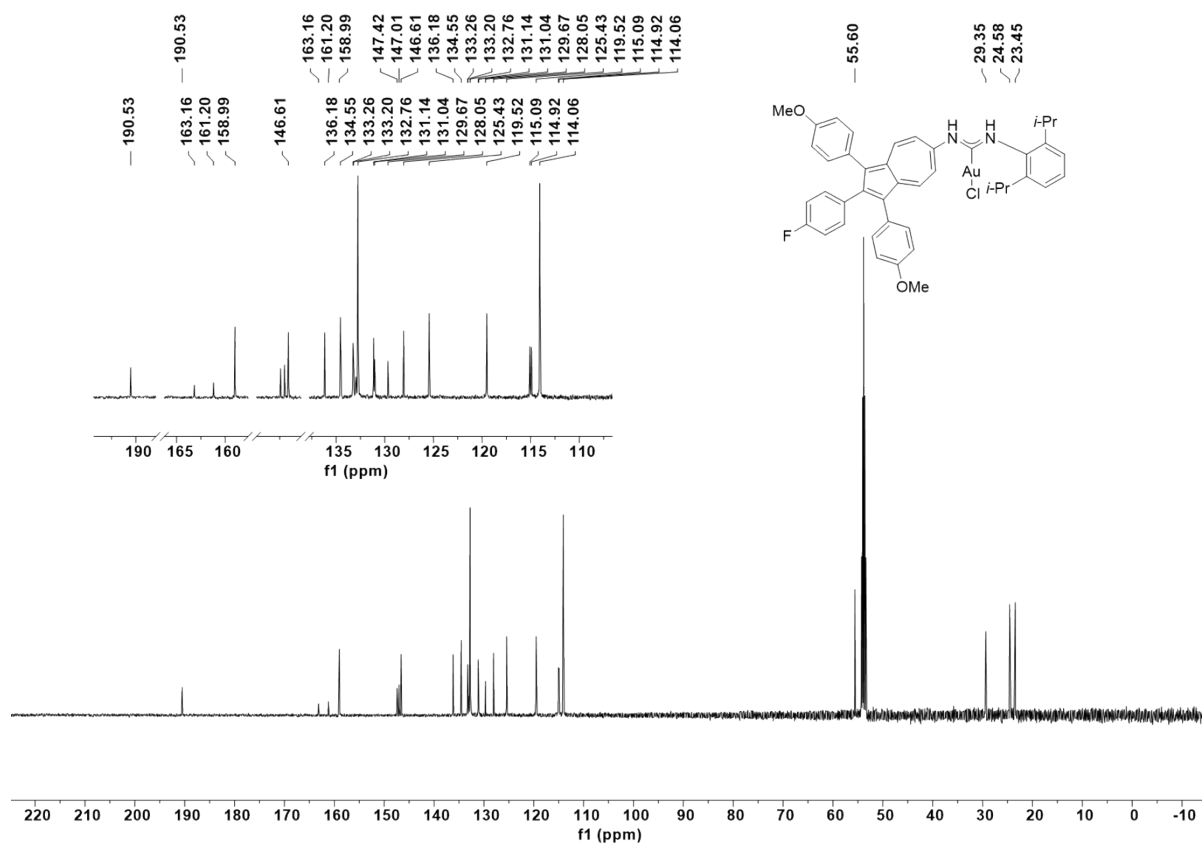


Figure S72. $^{13}\text{C}\{^{19}\text{F}, ^1\text{H}\}$ NMR Spectrum (126 MHz, CD_2Cl_2 , 295 K) of **14bf**.

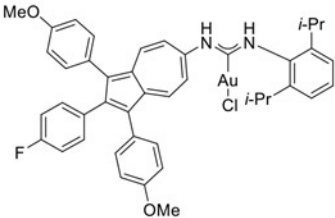


Figure S74. $^1\text{H}\{^{19}\text{F}\}$ NMR Spectrum (500 MHz, CD_2Cl_2 , 295 K) of **14bg.**

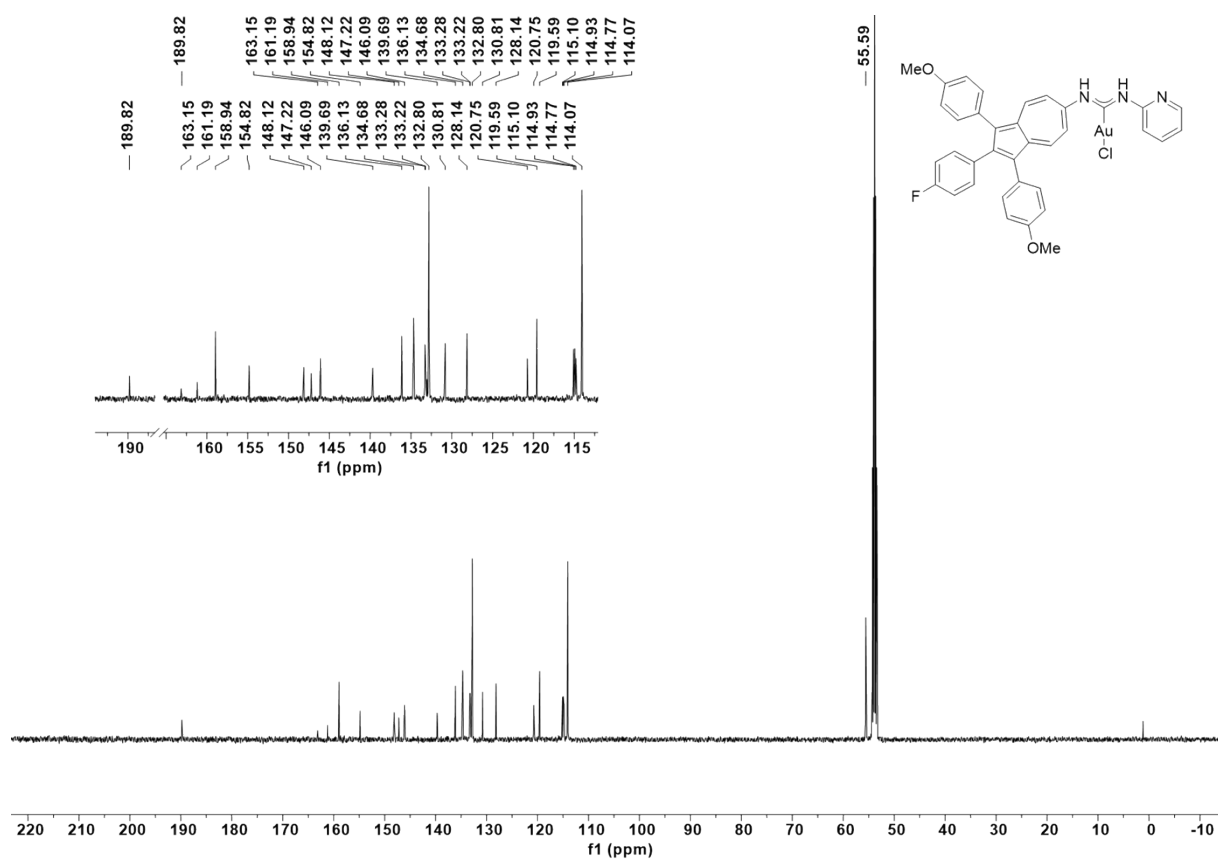


Figure S75. $^{13}\text{C}\{^{19}\text{F},^1\text{H}\}$ NMR Spectrum (126 MHz, CD_2Cl_2 , 295 K) of **14bg**.

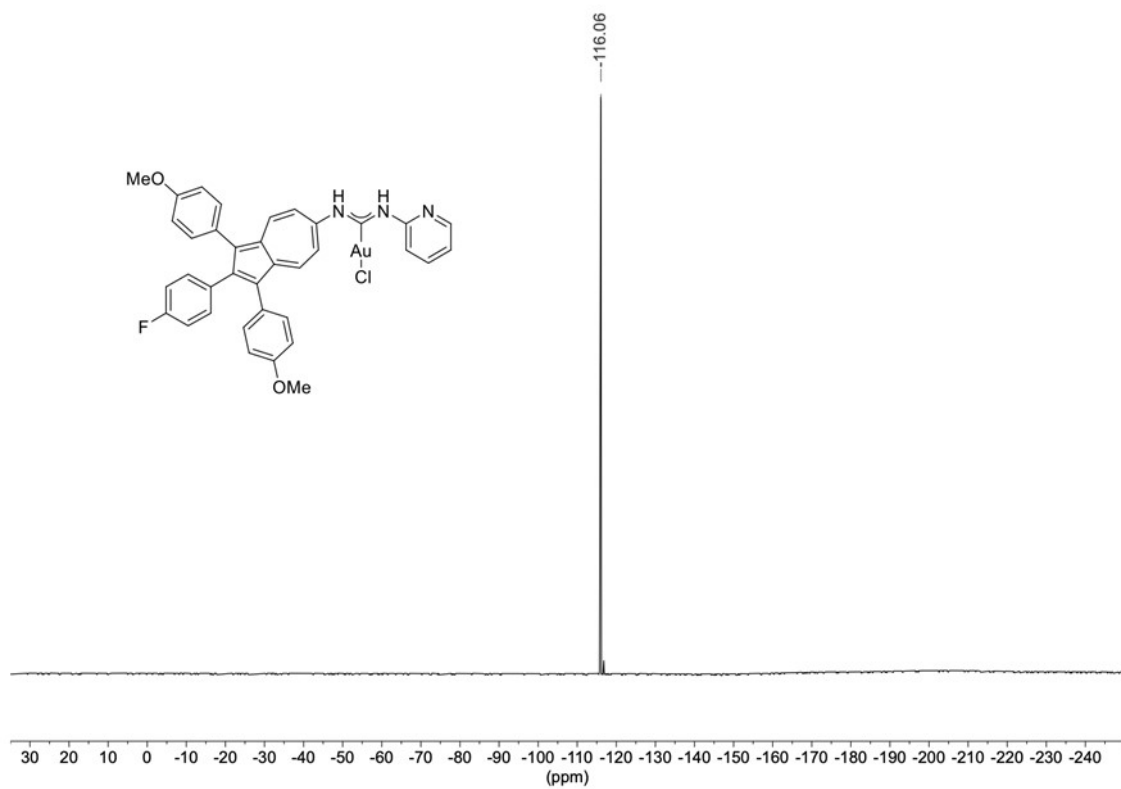


Figure S76. $^{19}\text{F}\{^1\text{H}\}$ NMR Spectrum (283 MHz, CD_2Cl_2 , 295 K) of **14bg**.

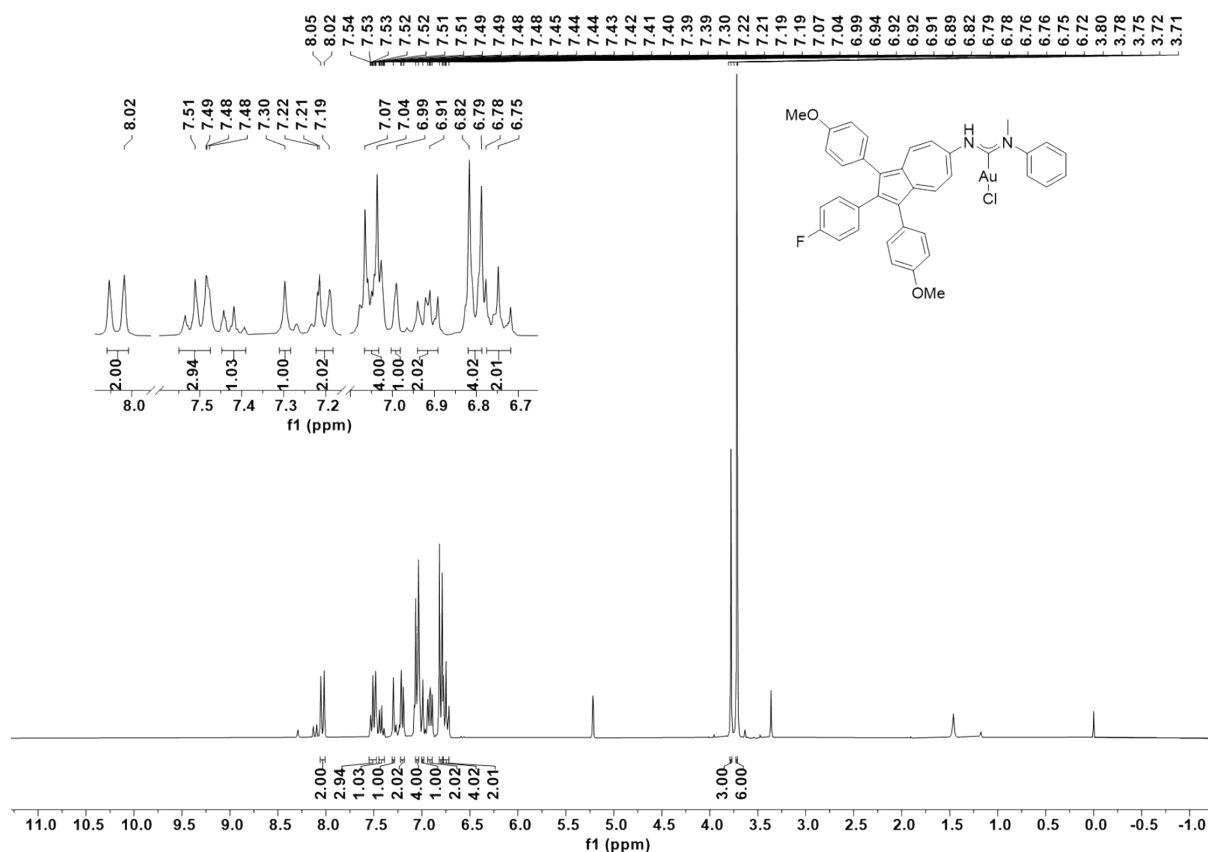


Figure S77. $^1\text{H}\{^{19}\text{F}\}$ NMR Spectrum (300 MHz, CD_2Cl_2 , 295 K) of **14bh**.

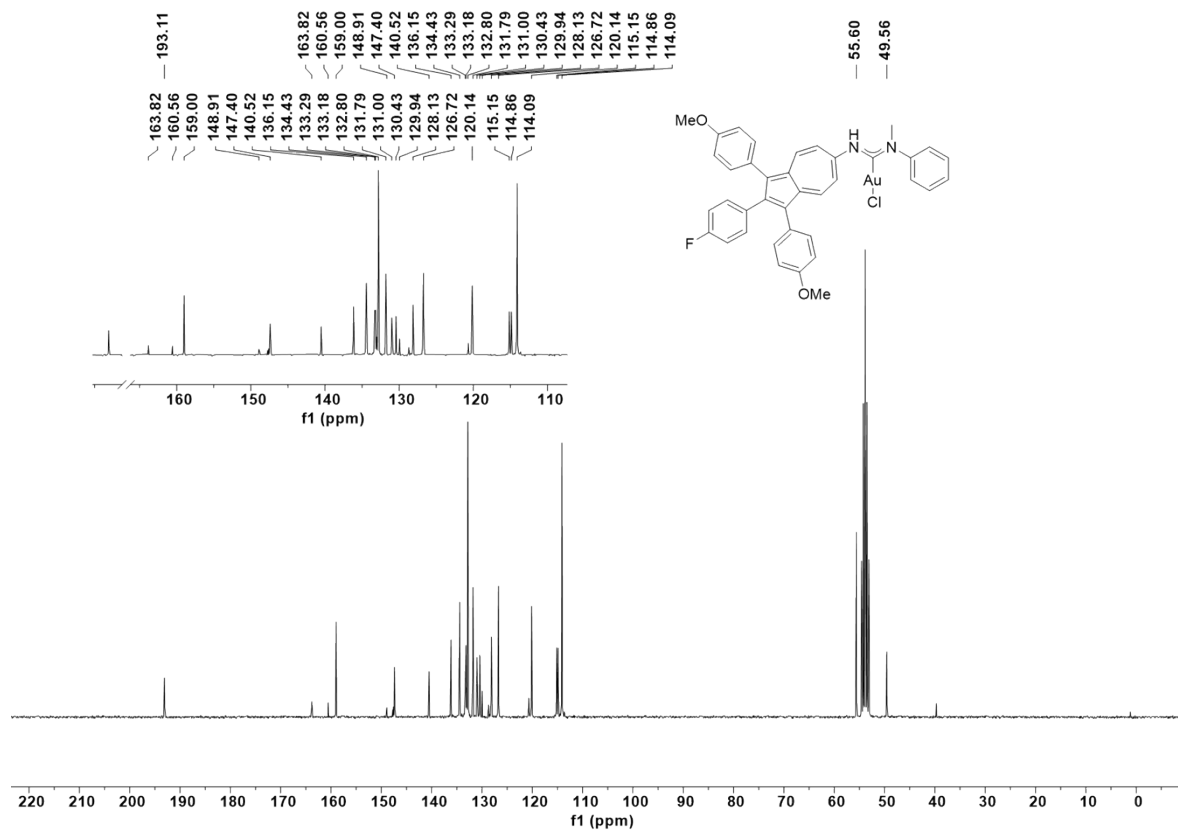


Figure S78. $^{13}\text{C}\{^{19}\text{F}, ^1\text{H}\}$ NMR Spectrum (75 MHz, CD_2Cl_2 , 295 K) of **14bh**.

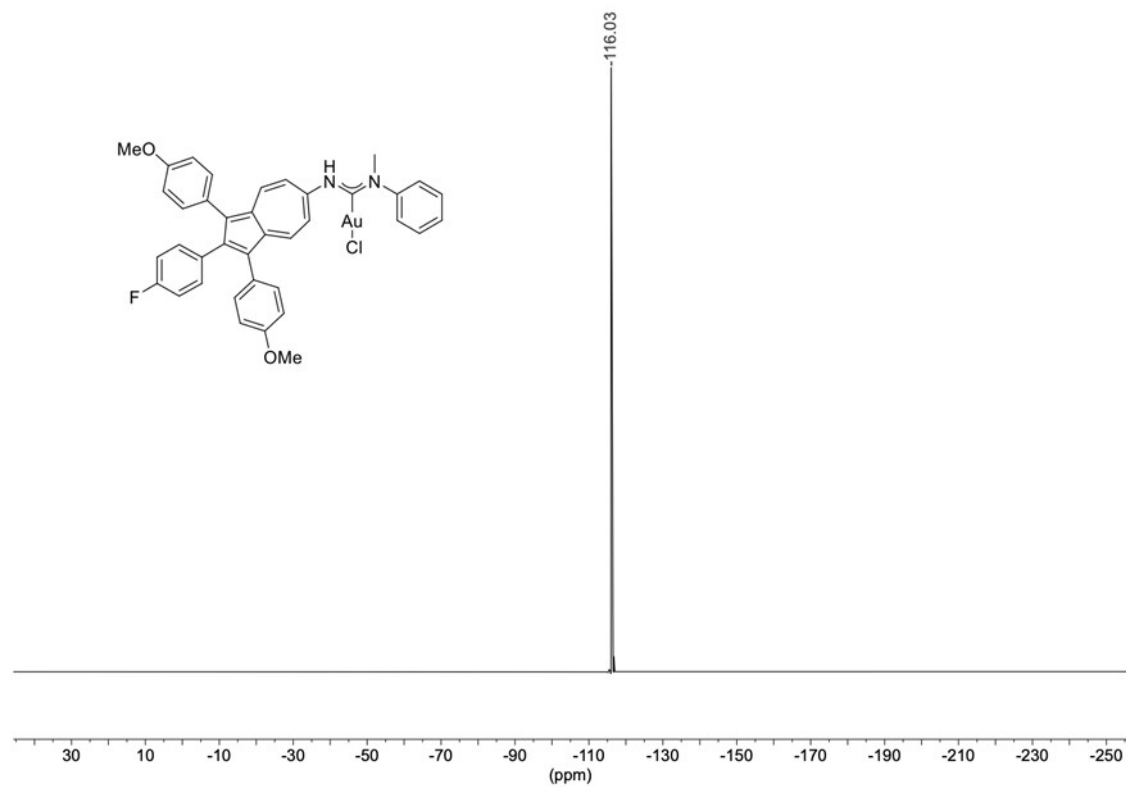


Figure S79. $^{19}\text{F}\{^1\text{H}\}$ NMR Spectrum (283 MHz, CD_2Cl_2 , 298 K) of **14bh**.

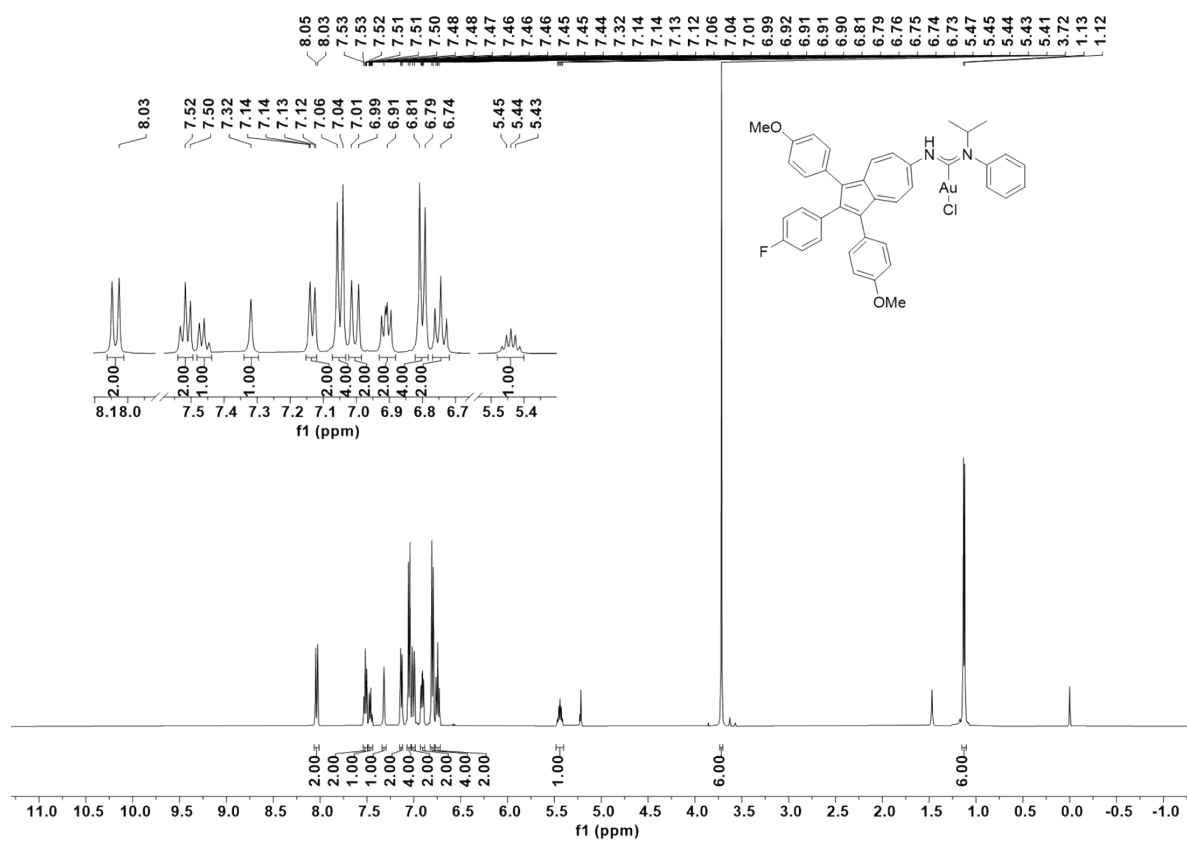
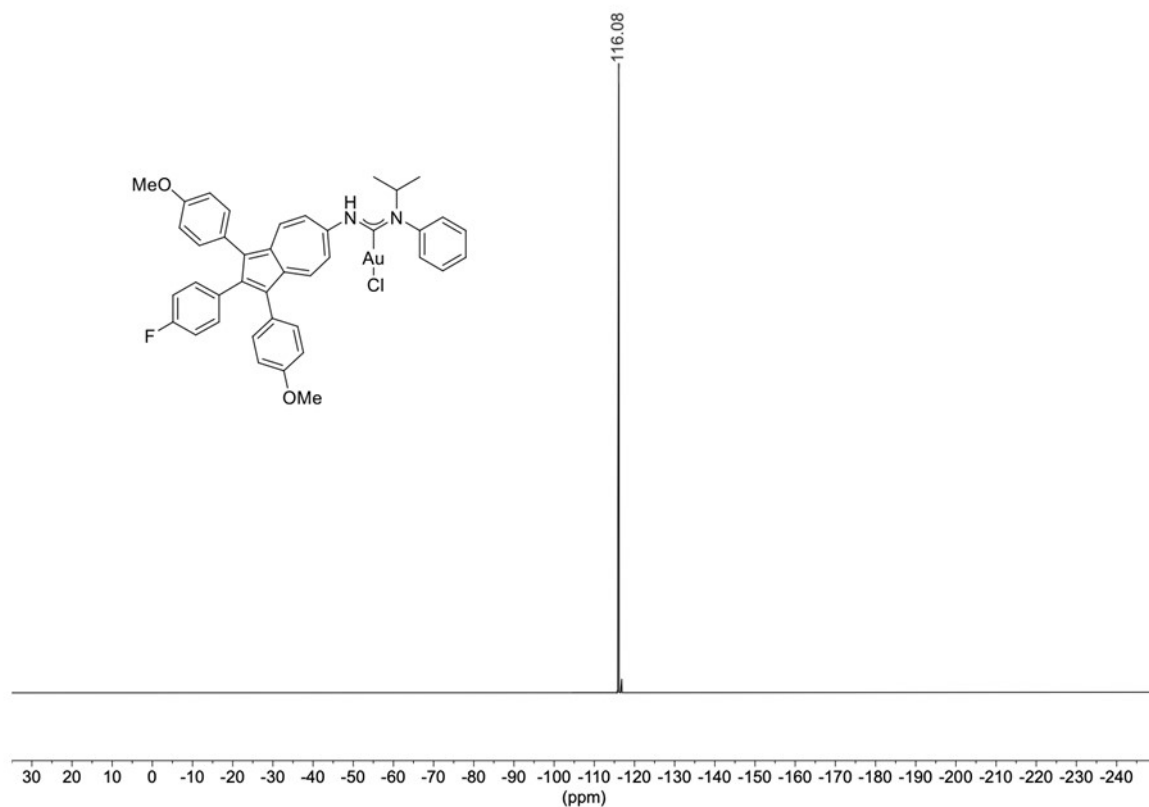
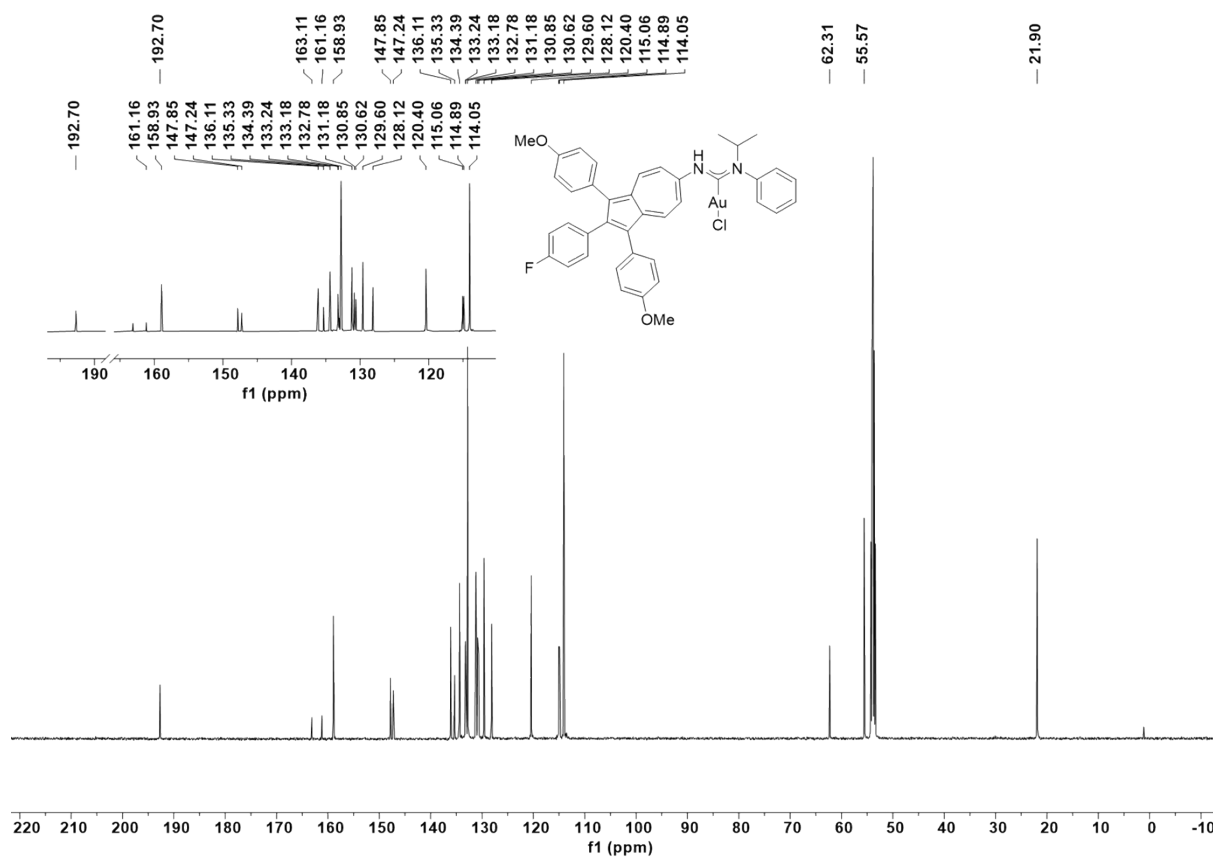
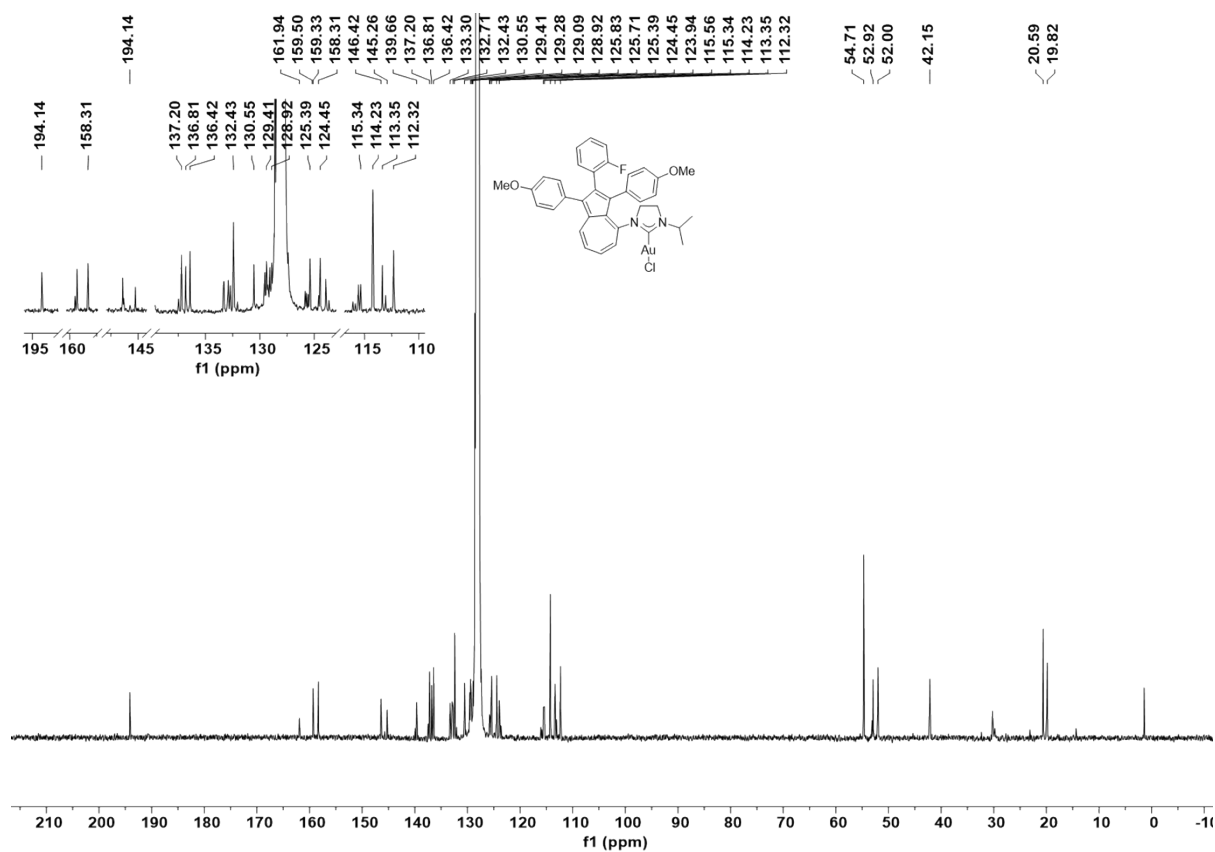
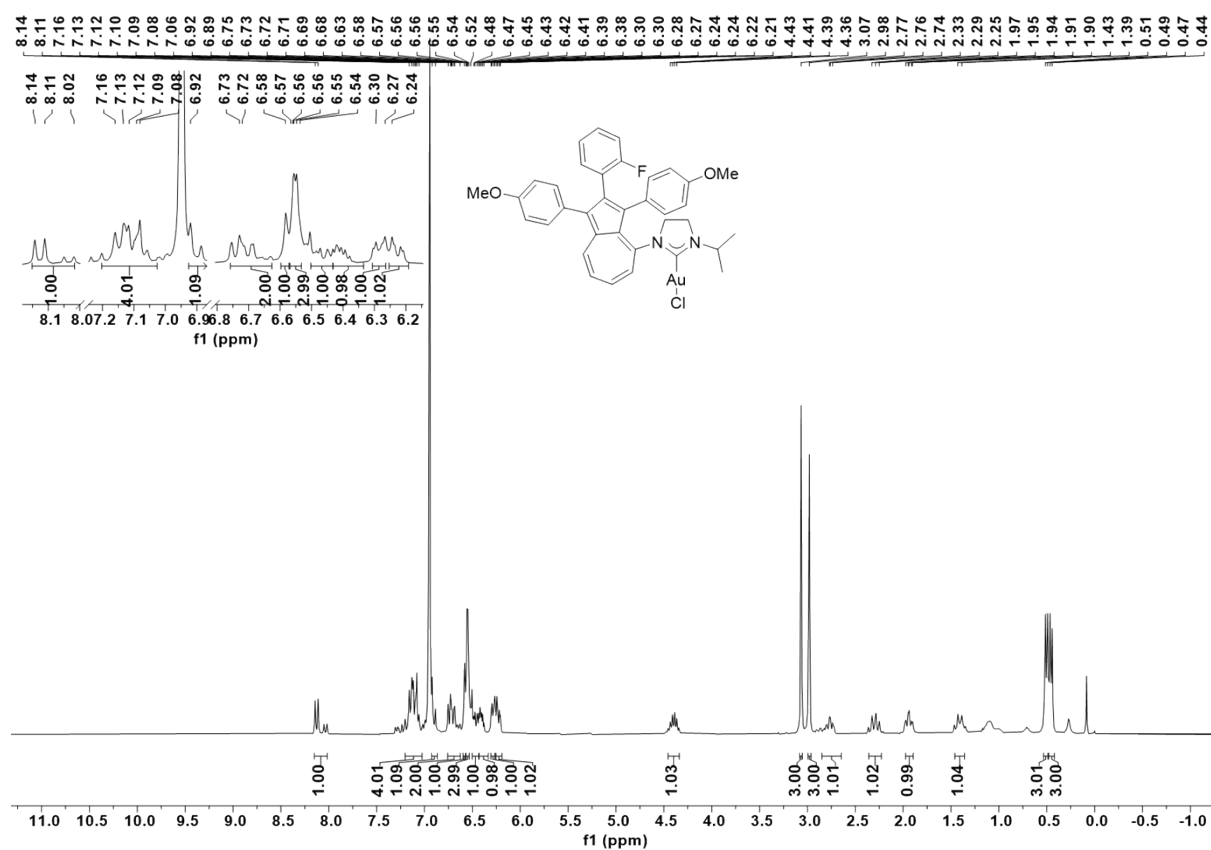


Figure S80. $^1\text{H}\{^{19}\text{F}\}$ NMR Spectrum (500 MHz, CD_2Cl_2 , 295 K) of **14bi**.





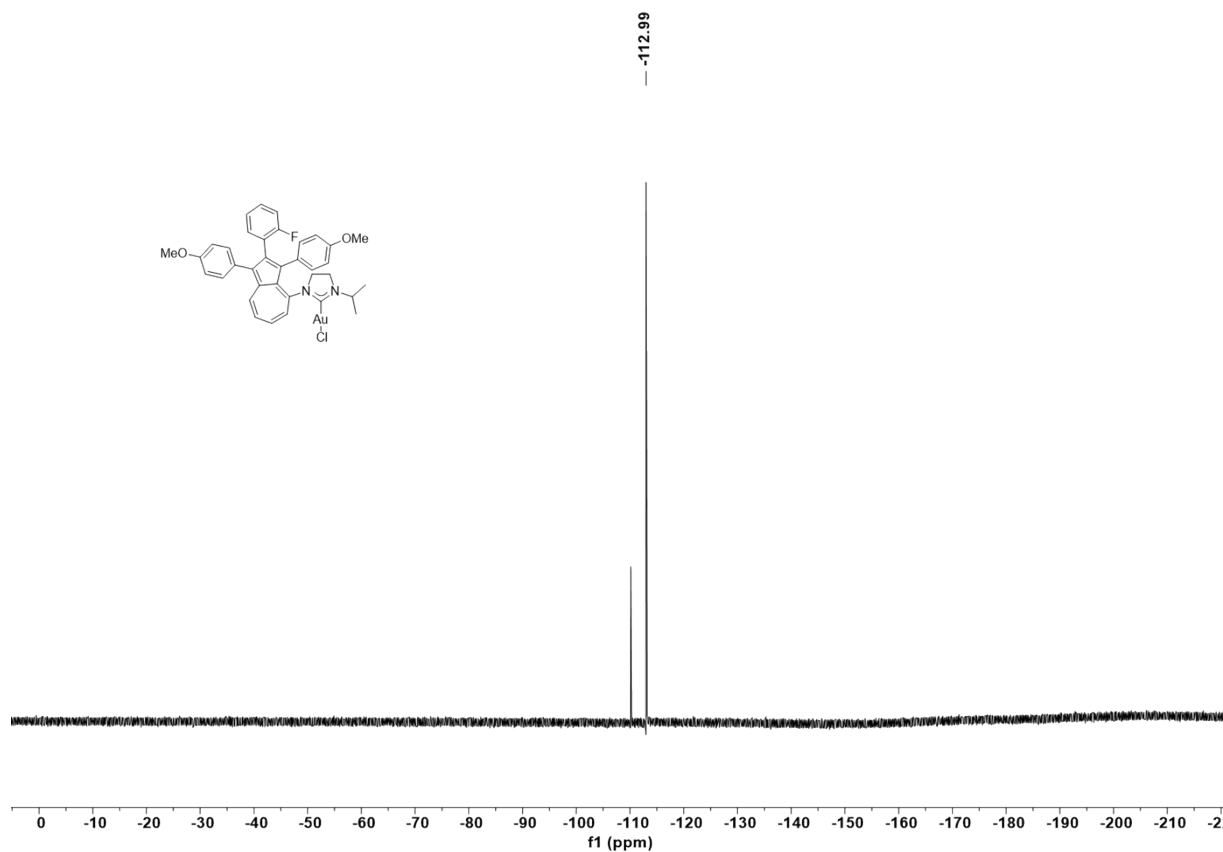


Figure S85. $^{19}\text{F}\{^1\text{H}\}$ NMR Spectrum (283 MHz, C_6D_6 , 295 K) of **16a**.

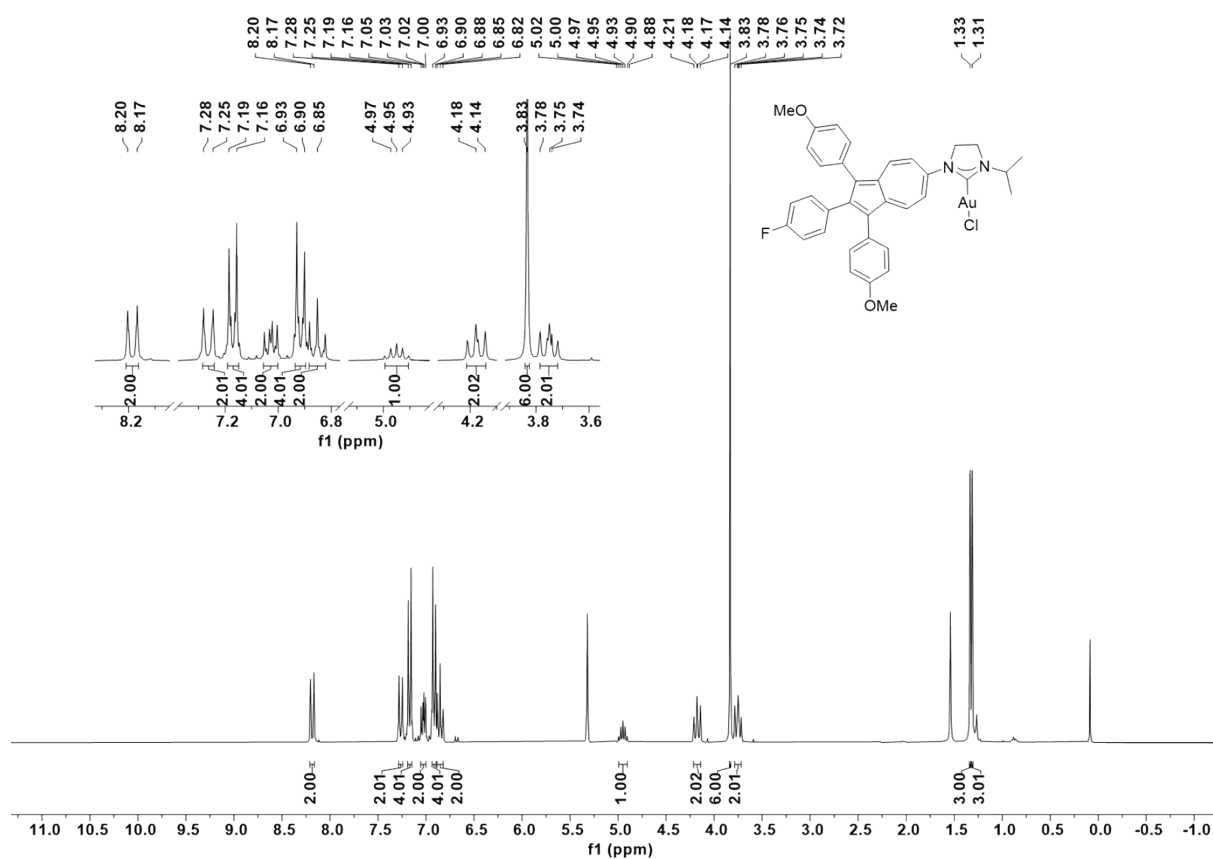


Figure S86. $^1\text{H}\{^{19}\text{F}\}$ NMR Spectrum (300 MHz, CD_2Cl_2 , 295 K) of **16b**.

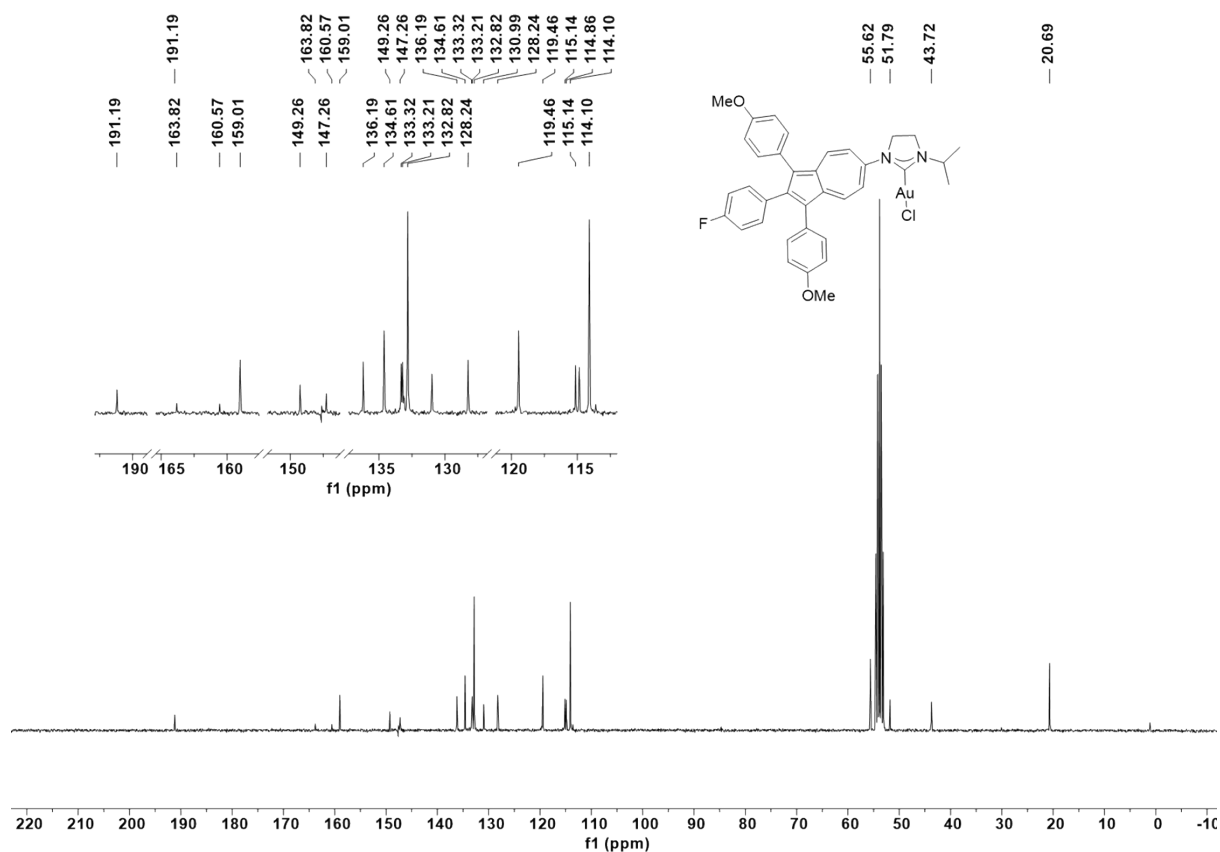


Figure S87. $^{13}\text{C}\{^{19}\text{F},^1\text{H}\}$ NMR Spectrum (75 MHz, CD_2Cl_2 , 295 K) of **16b**.

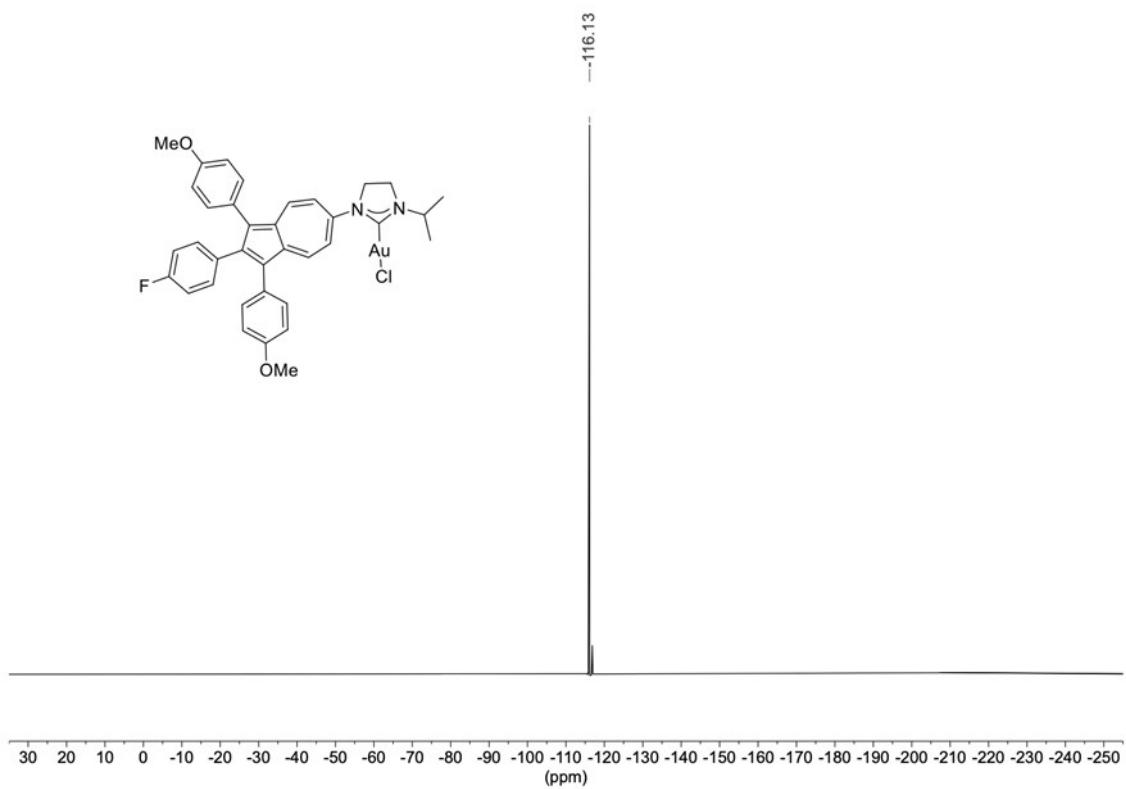


Figure S88. $^{19}\text{F}\{^1\text{H}\}$ NMR Spectrum (283 MHz, CD_2Cl_2 , 298 K) of **16b**.

5 IR Spectra

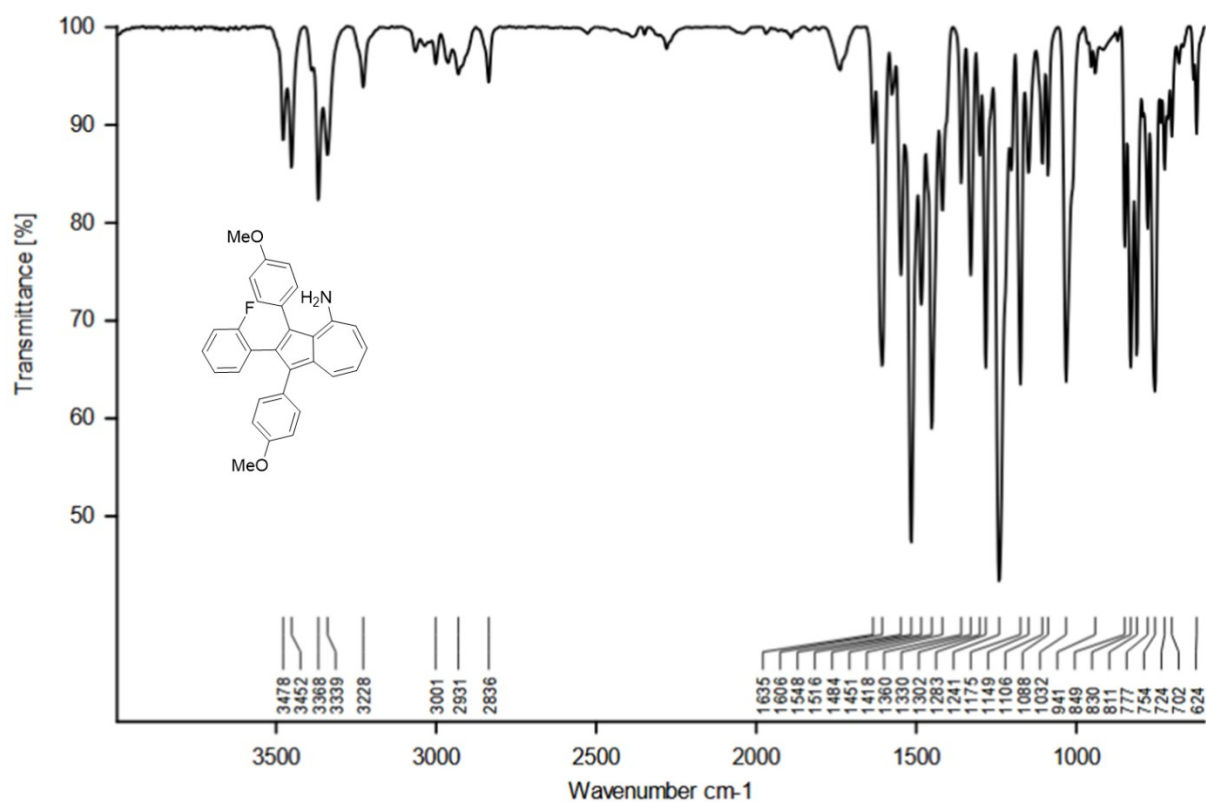


Figure S89. IR (ATR) Spectrum of 4a.

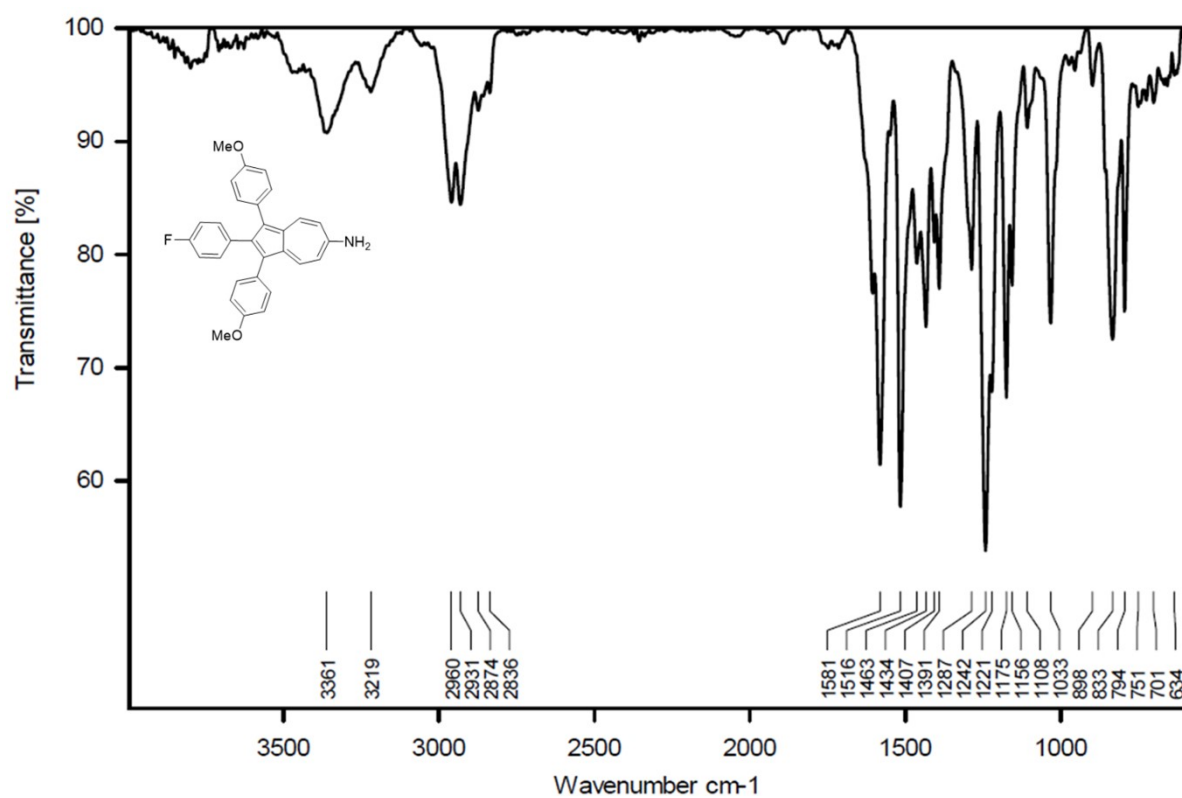


Figure S90. IR (ATR) Spectrum of 4b.

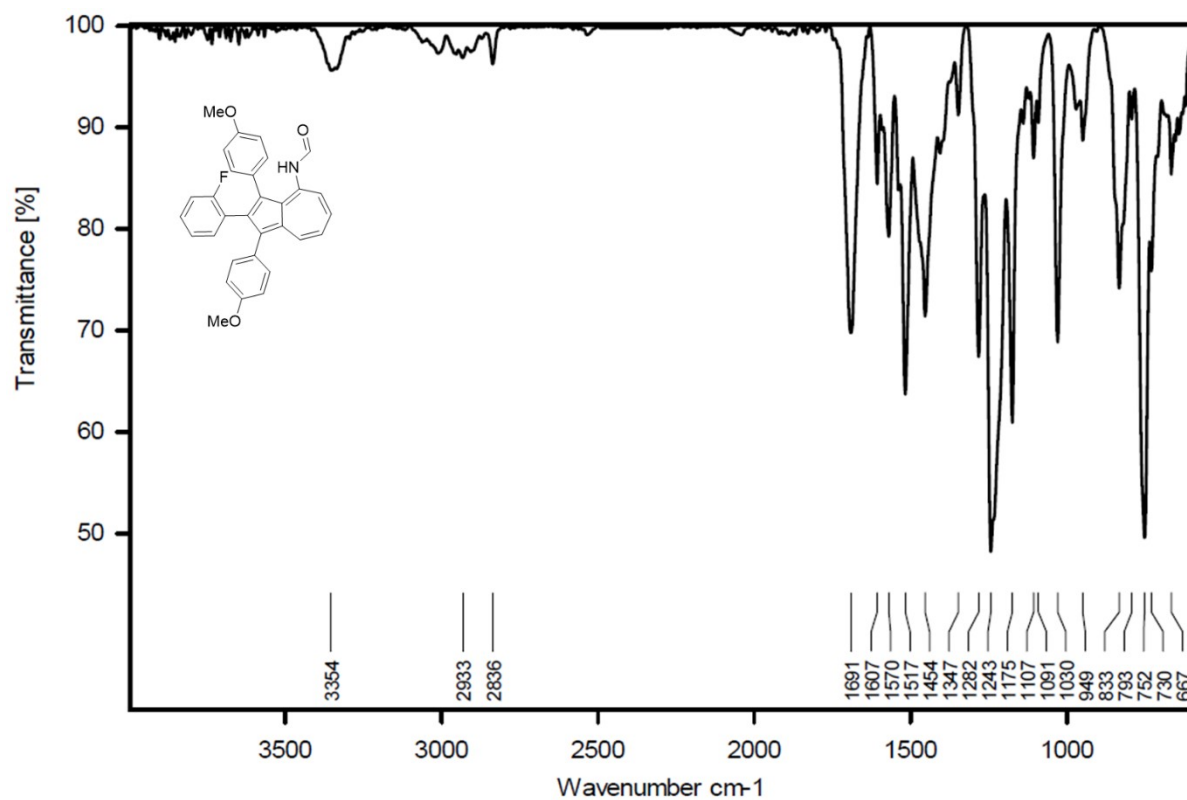


Figure S91. IR (ATR) Spectrum of **6a**.

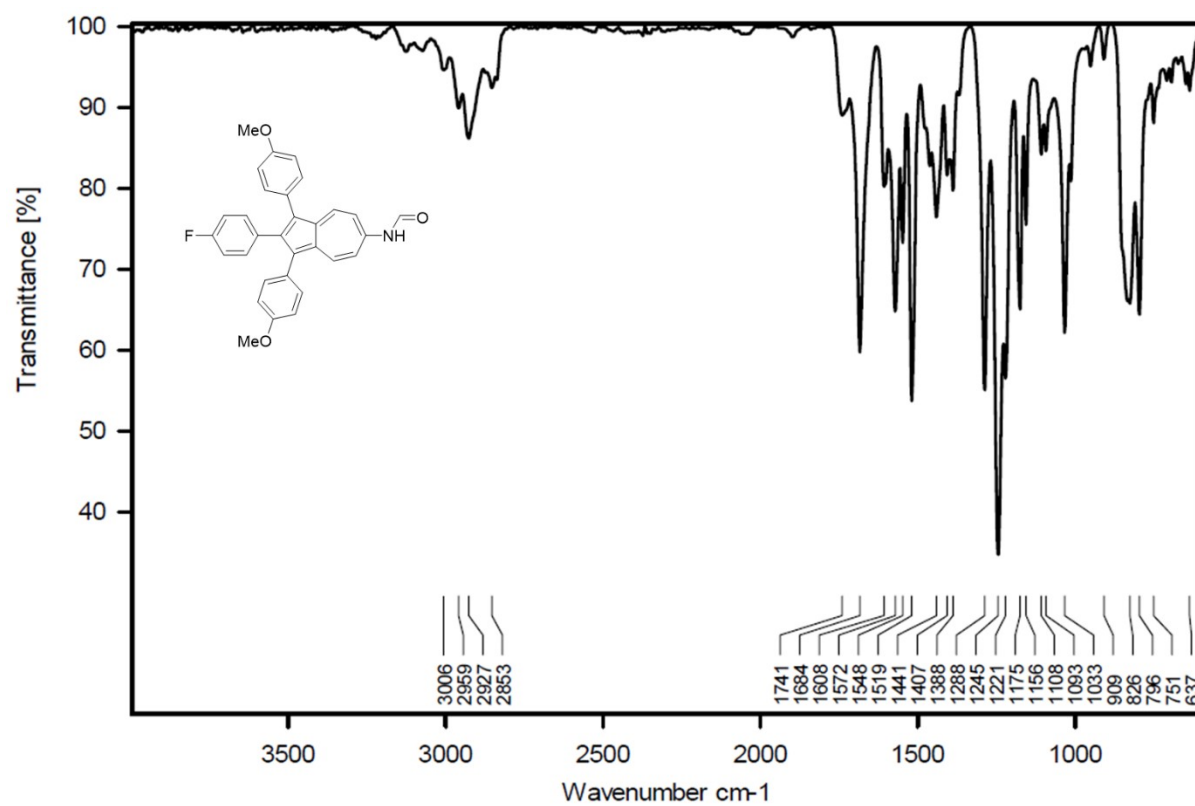


Figure S92. IR (ATR) Spectrum of **6b**.

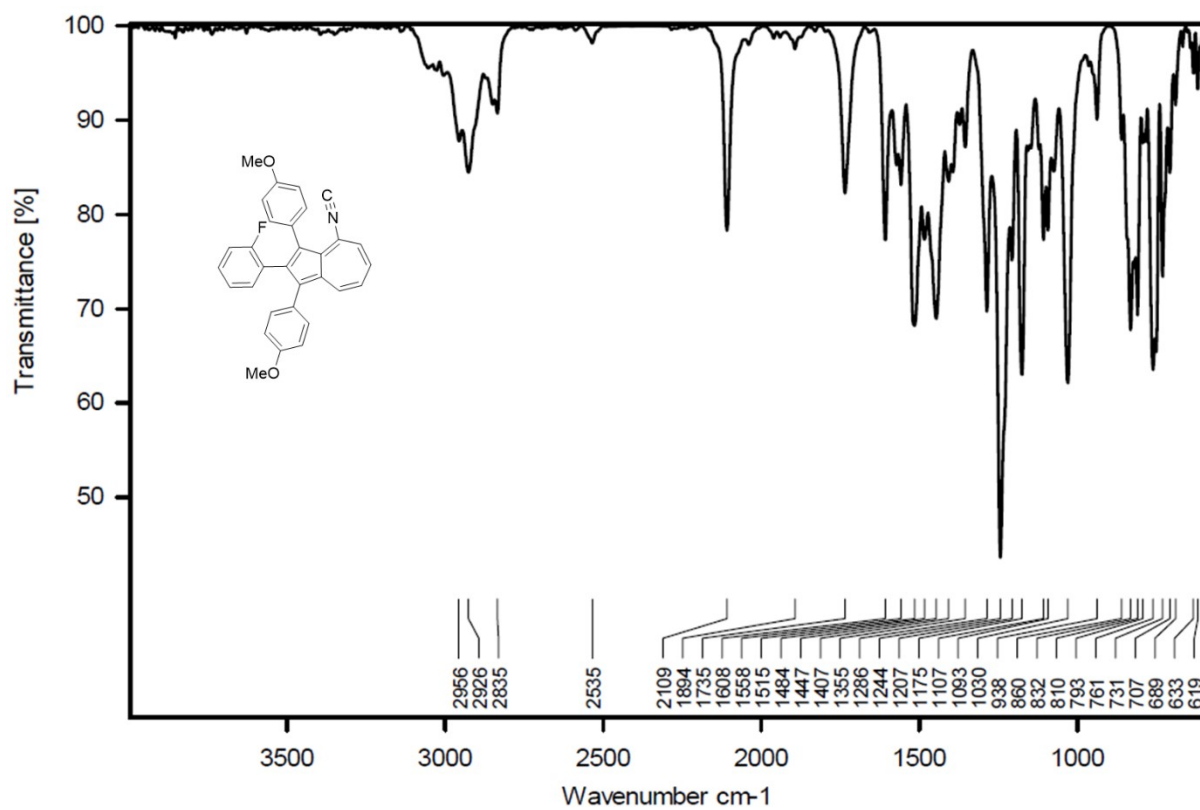


Figure S93. IR (ATR) Spectrum of **10a**.

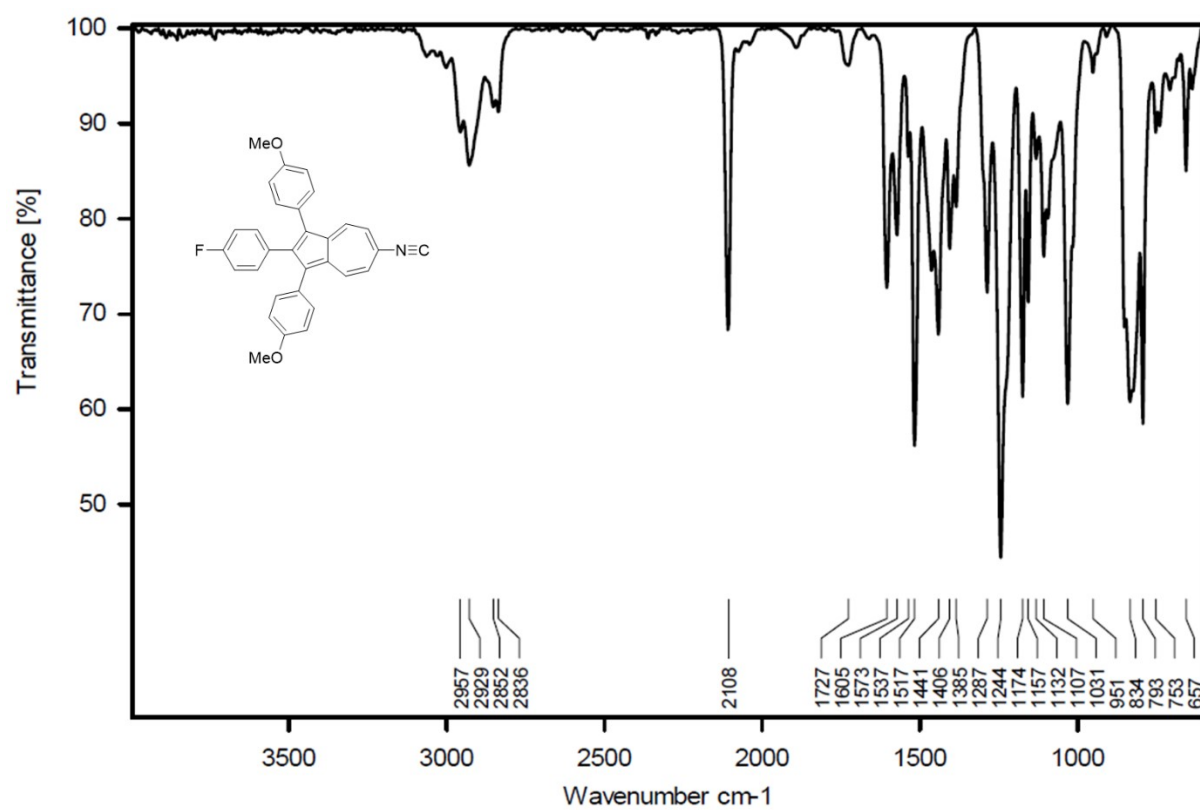


Figure S94. IR (ATR) Spectrum of **10b**.

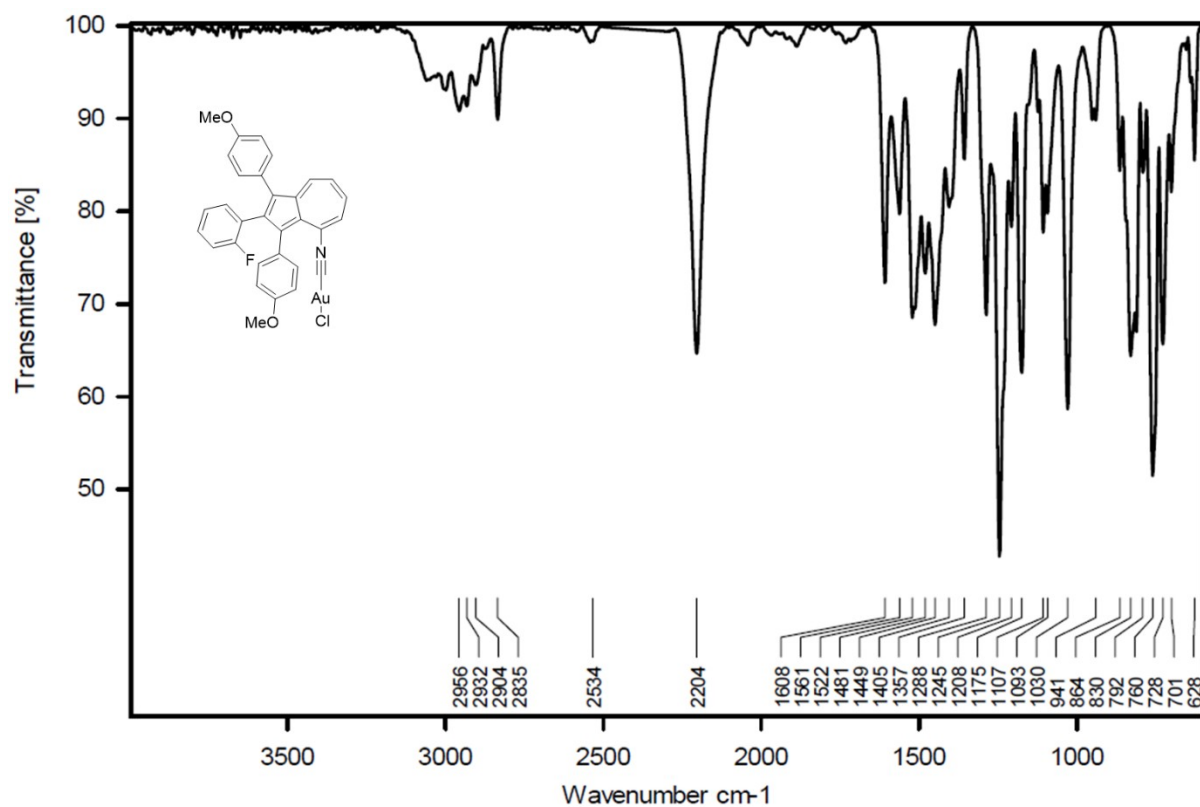


Figure S95. IR (ATR) Spectrum of 12a.

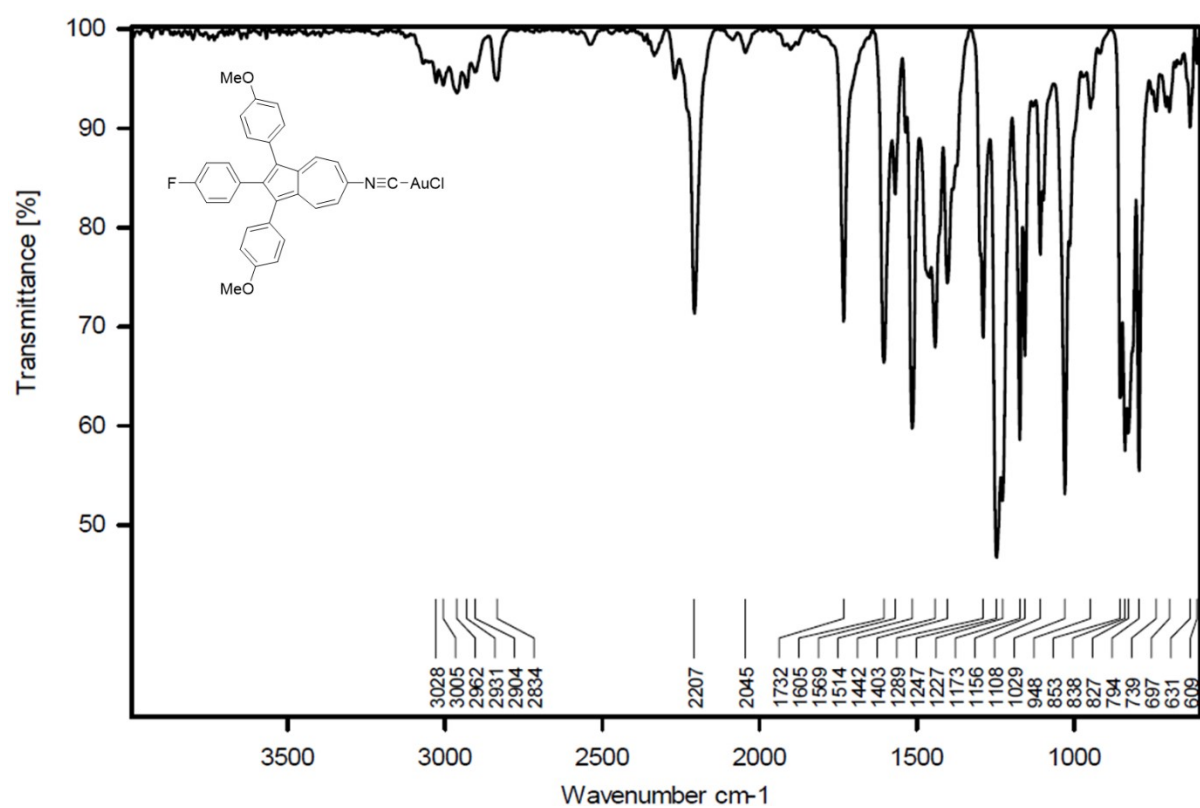


Figure S96. IR (ATR) Spectrum of 12b.

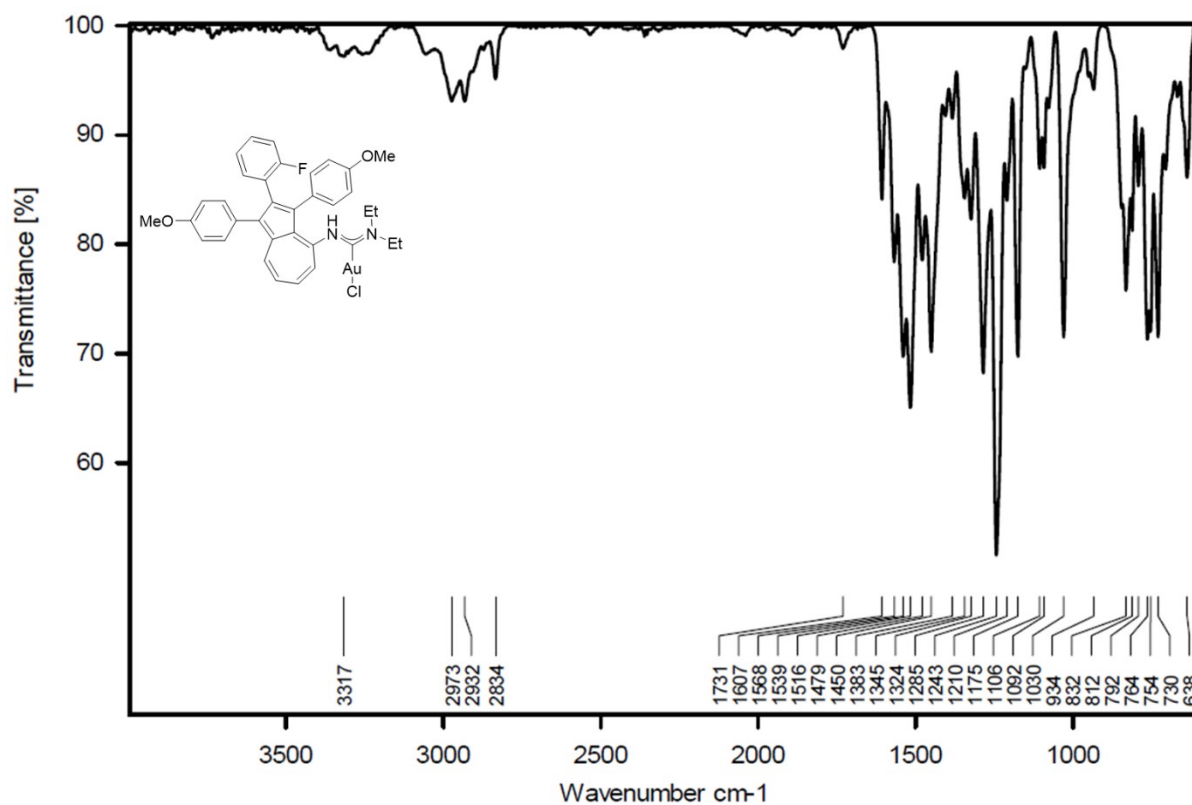


Figure S97. IR (ATR) Spectrum of **14aa**.

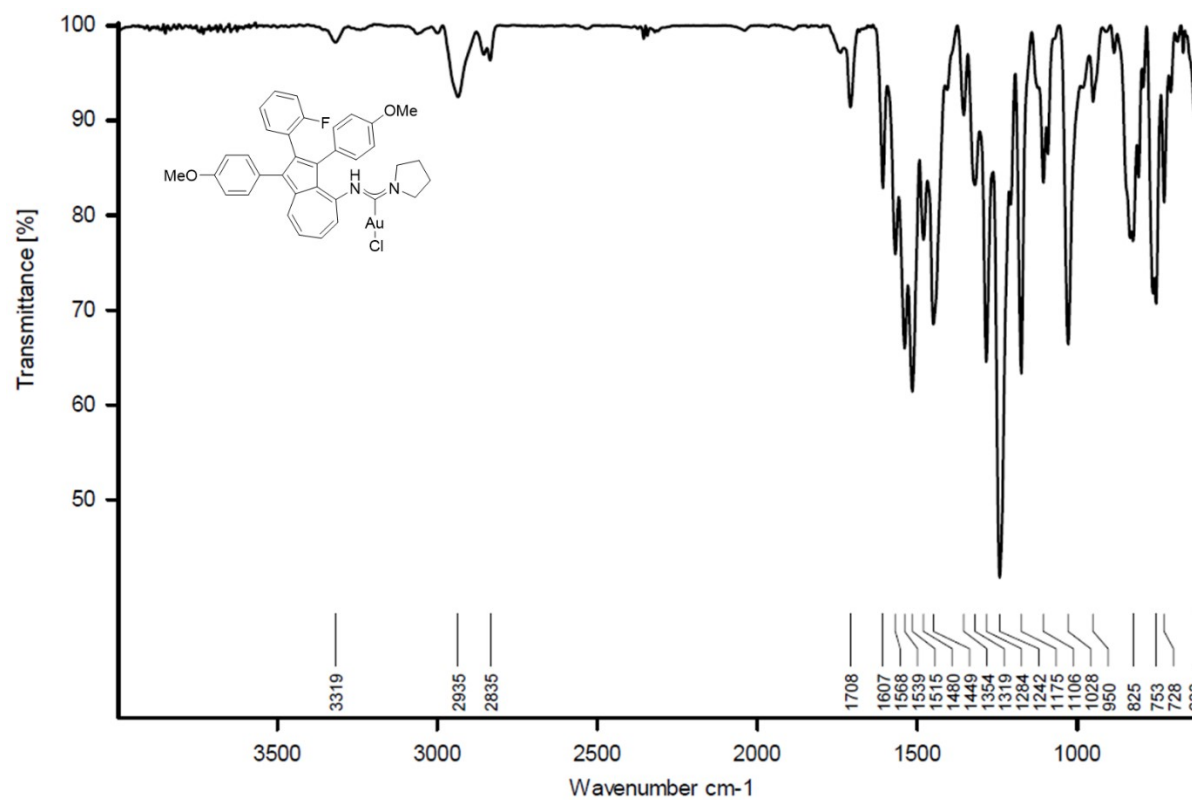


Figure S98. IR (ATR) Spectrum of **14ab**.

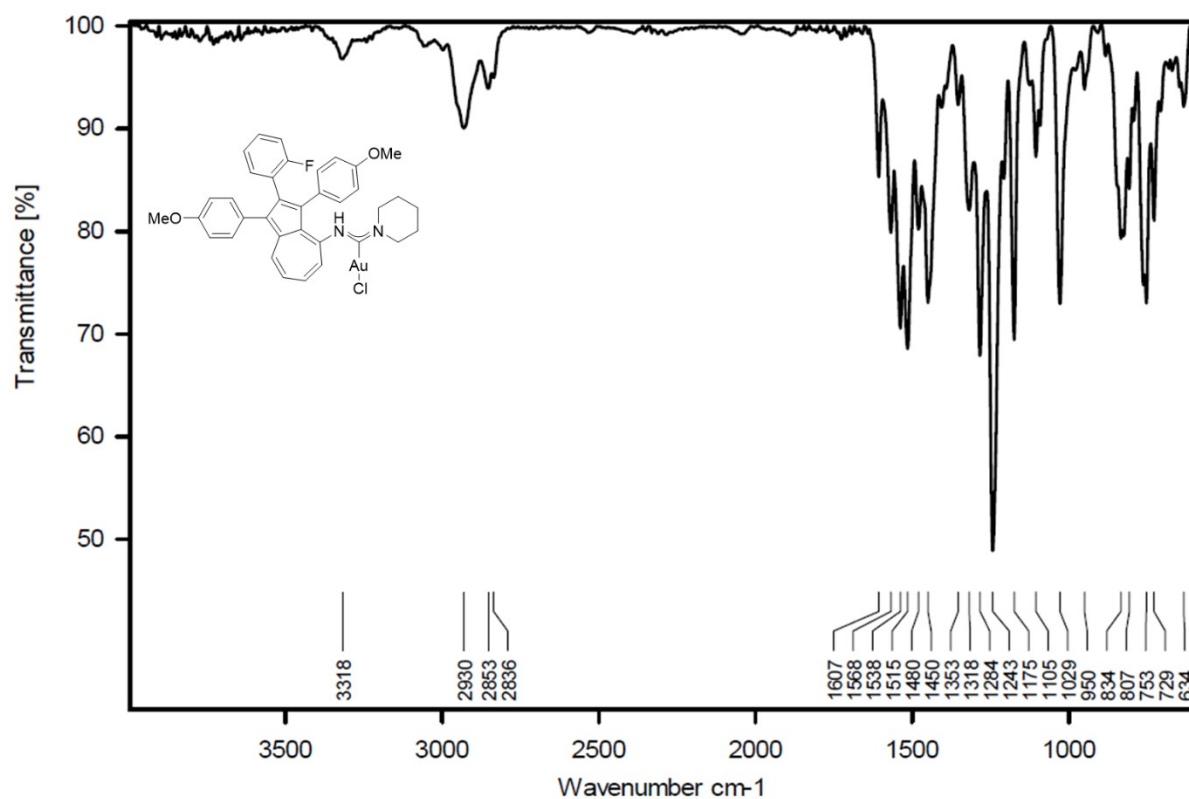


Figure S99. IR (ATR) Spectrum of **14ac**.

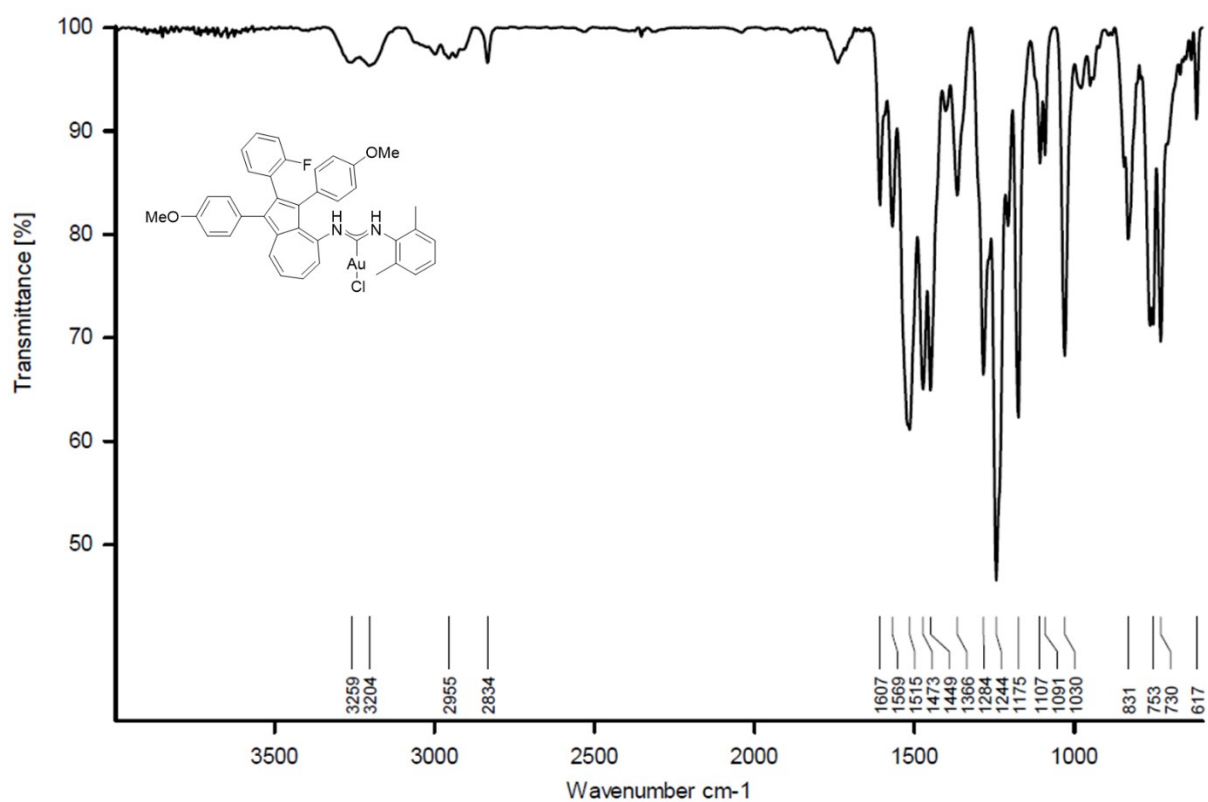


Figure S100. IR (ATR) Spectrum of **14ad**.

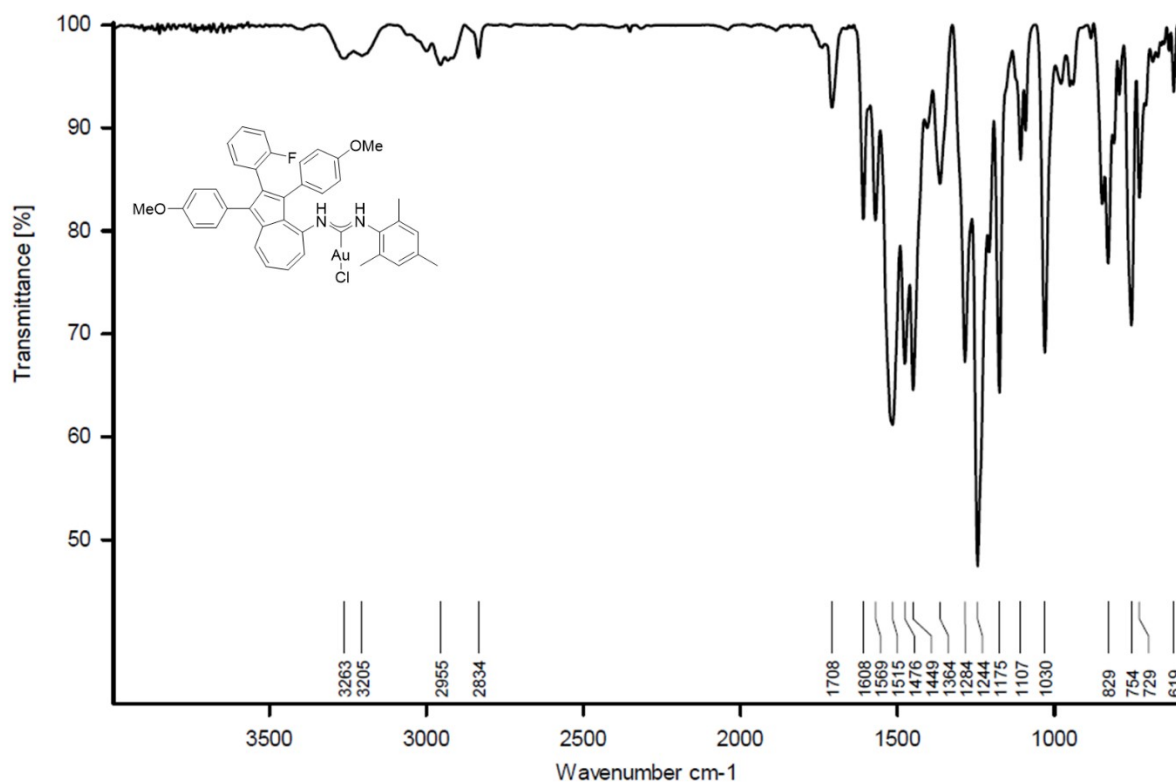


Figure S101. IR (ATR) Spectrum of **14ae**.

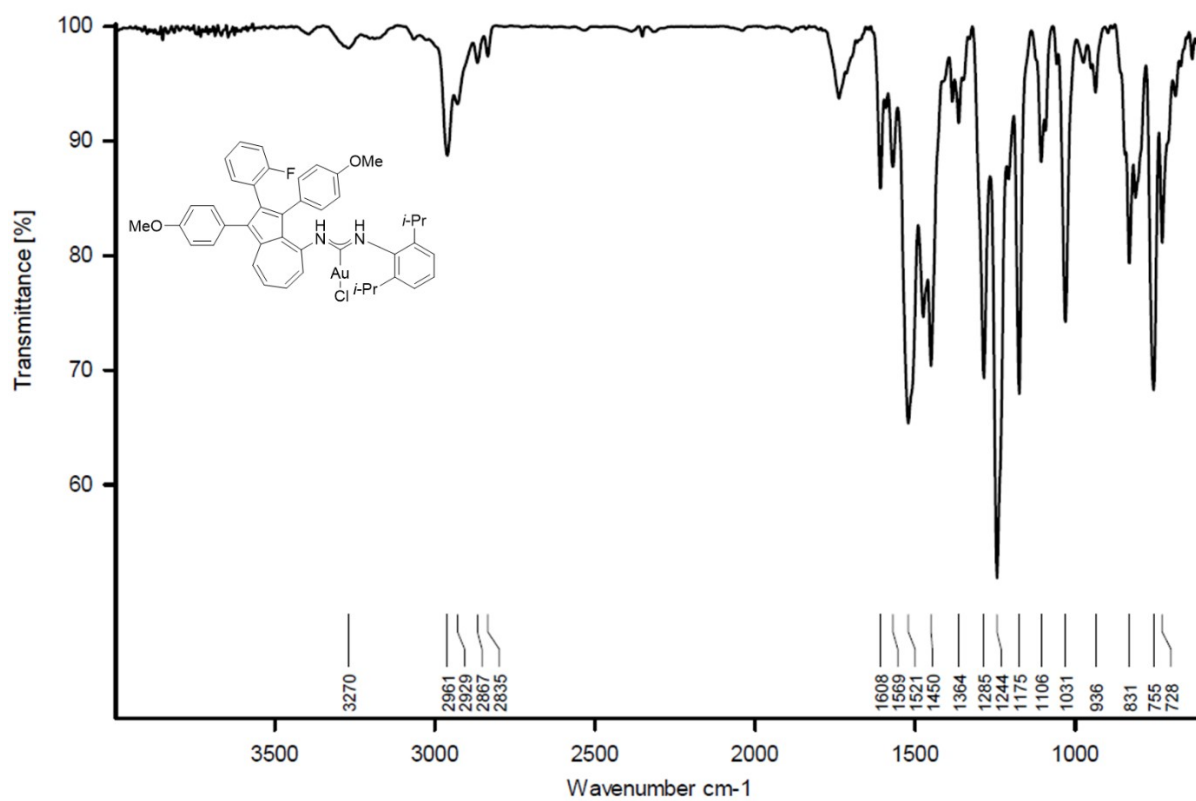


Figure S102. IR (ATR) Spectrum of **14af**.

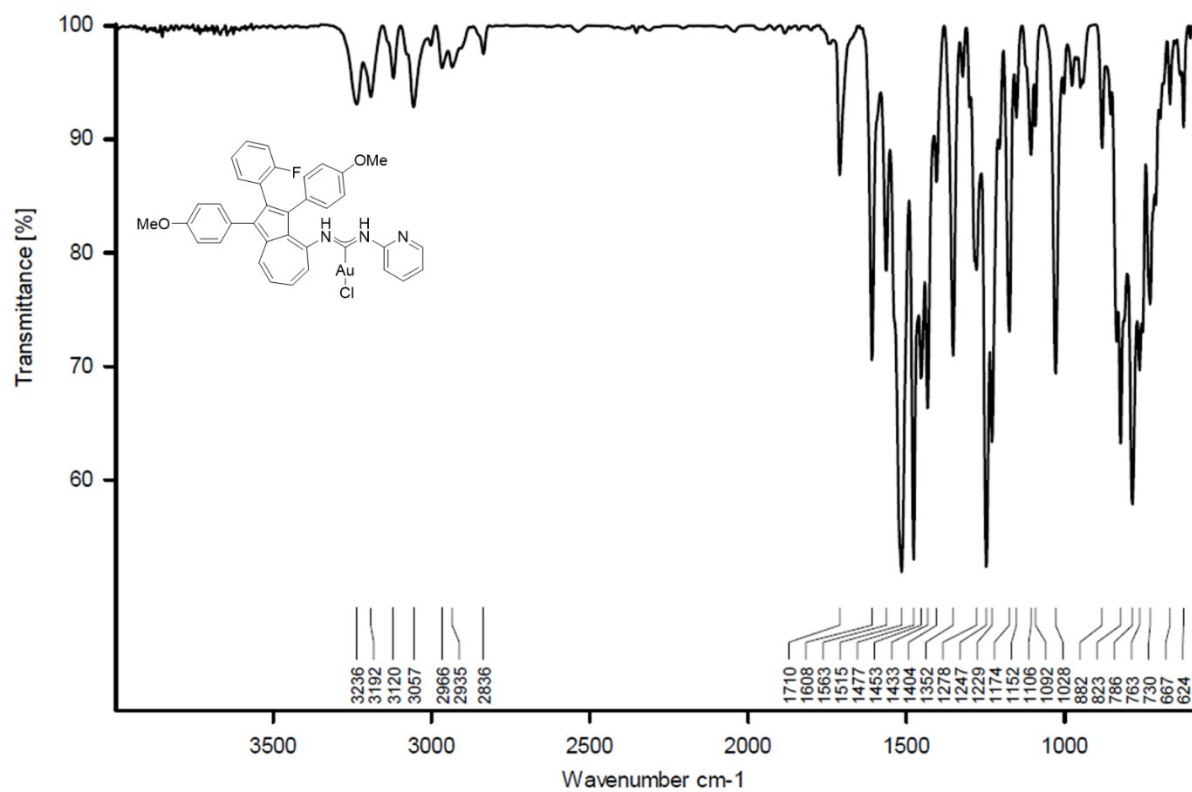


Figure S103. IR (ATR) Spectrum of **14ag**.

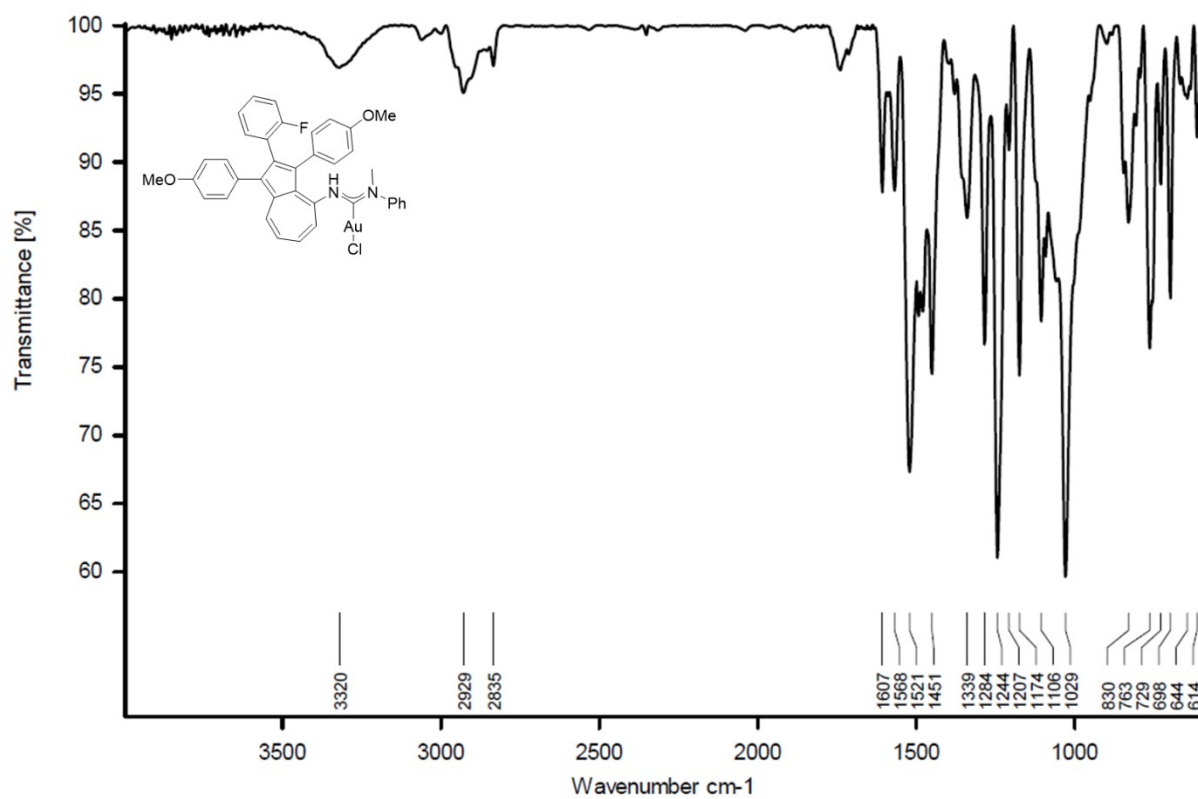


Figure S104. IR (ATR) Spectrum of **14ah**.

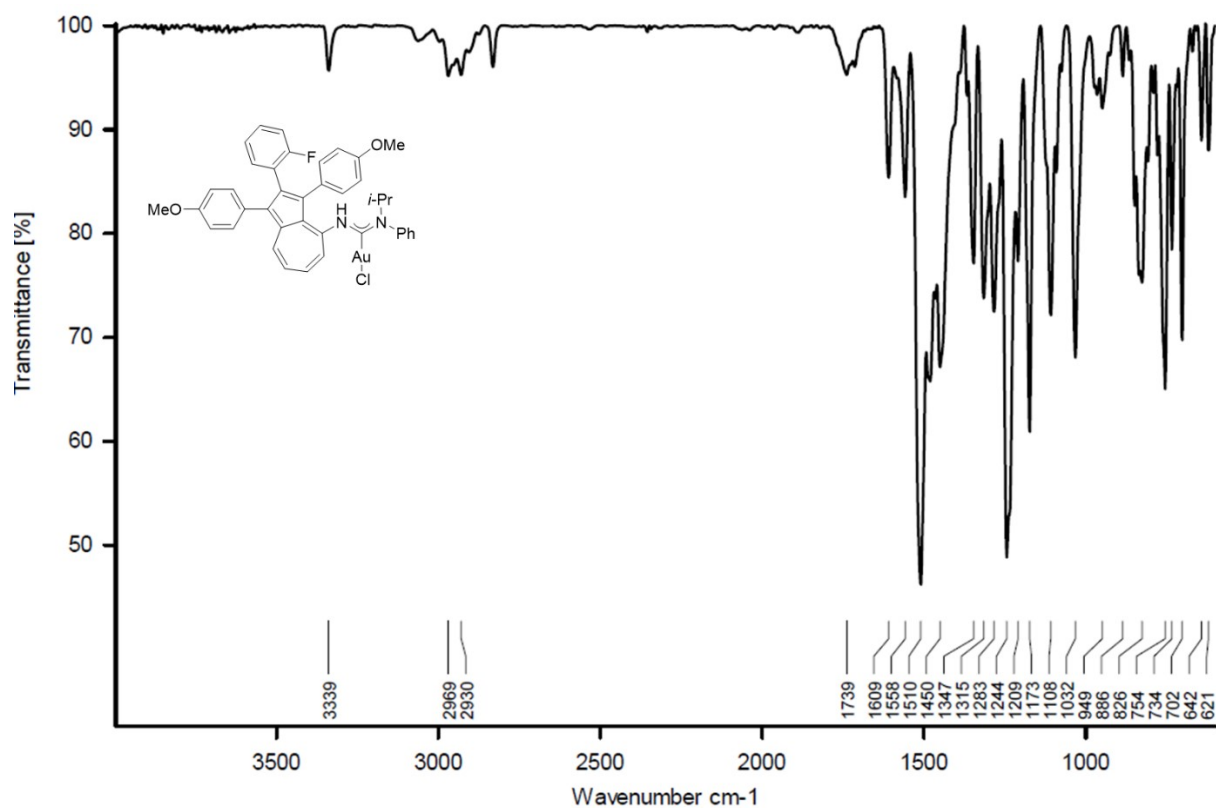


Figure S105. IR (ATR) Spectrum of **14ai**.

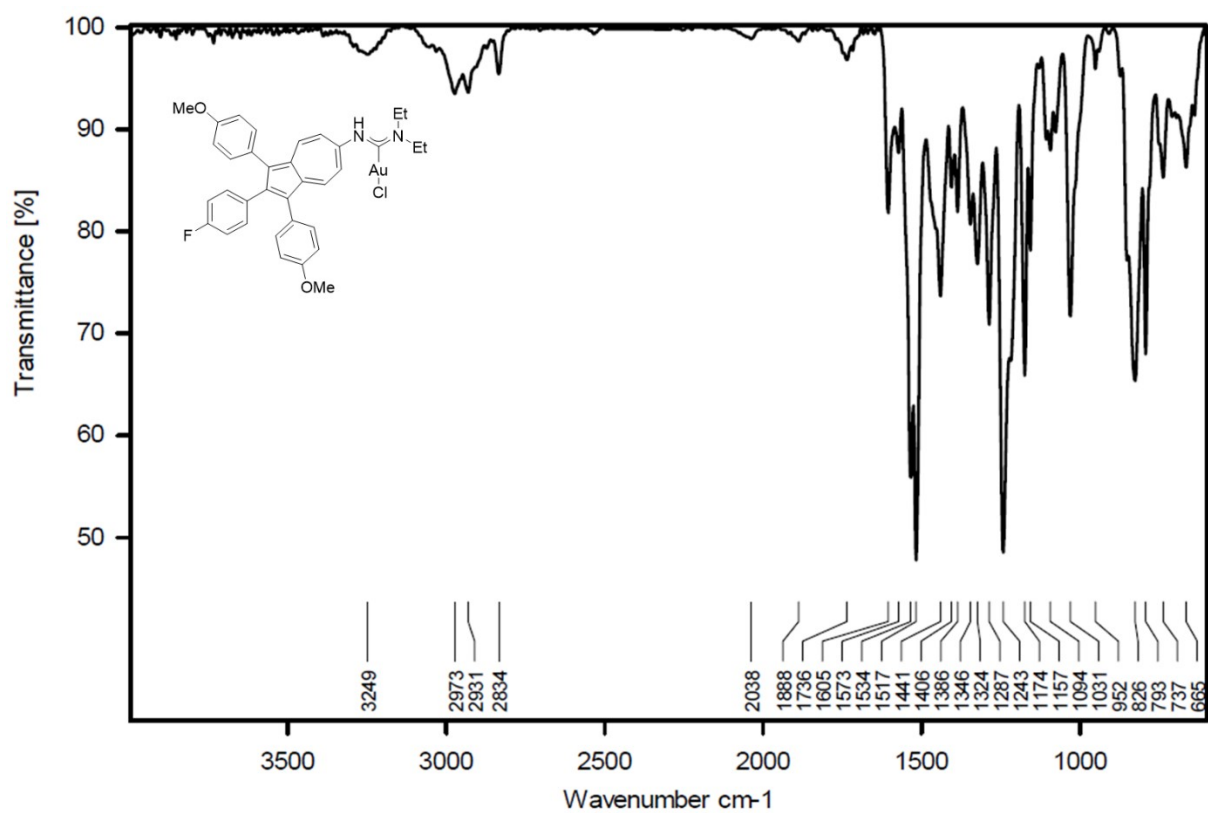


Figure S106. IR (ATR) Spectrum of **14ba**.

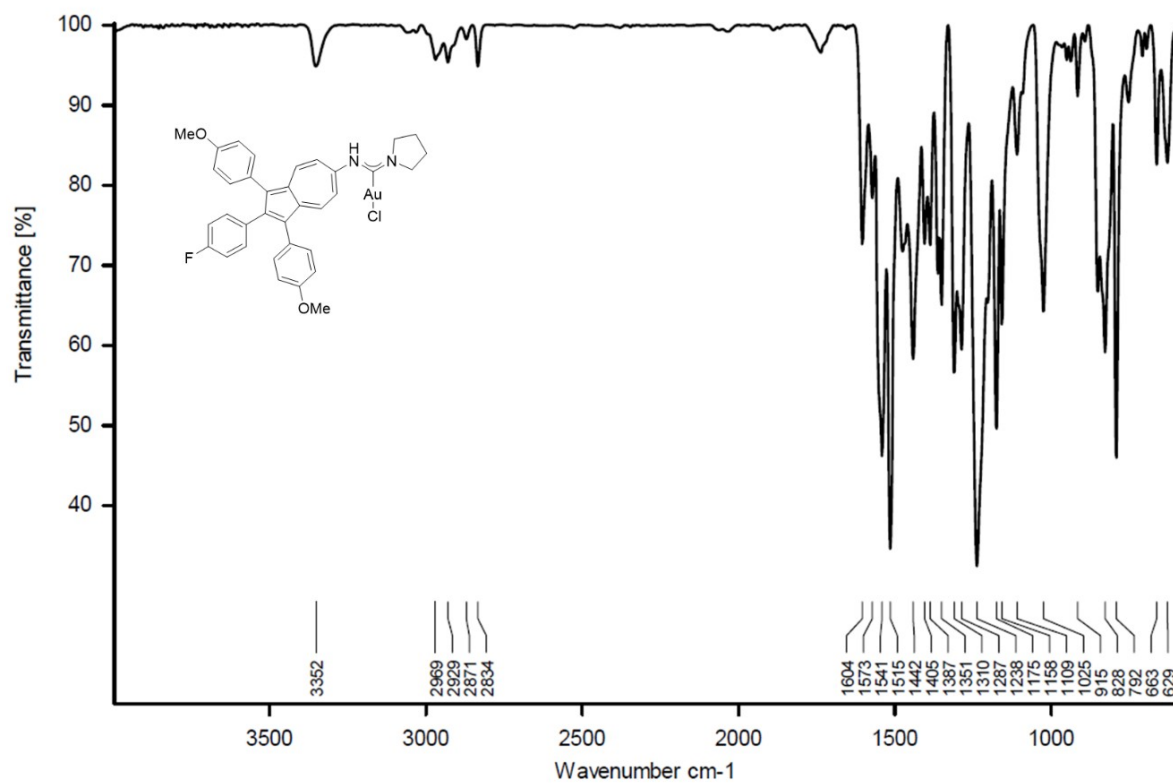


Figure S107. IR (ATR) Spectrum of **14bb**.

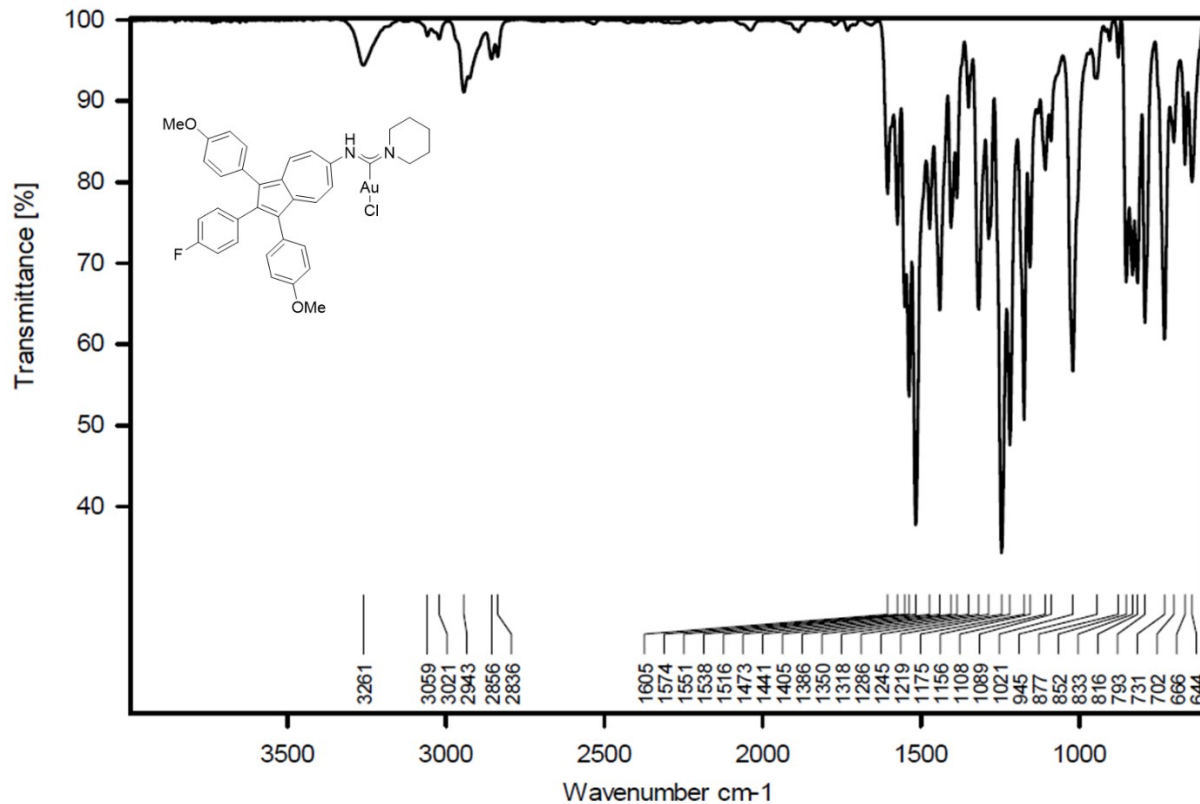


Figure S108. IR (ATR) Spectrum of **14bc**.

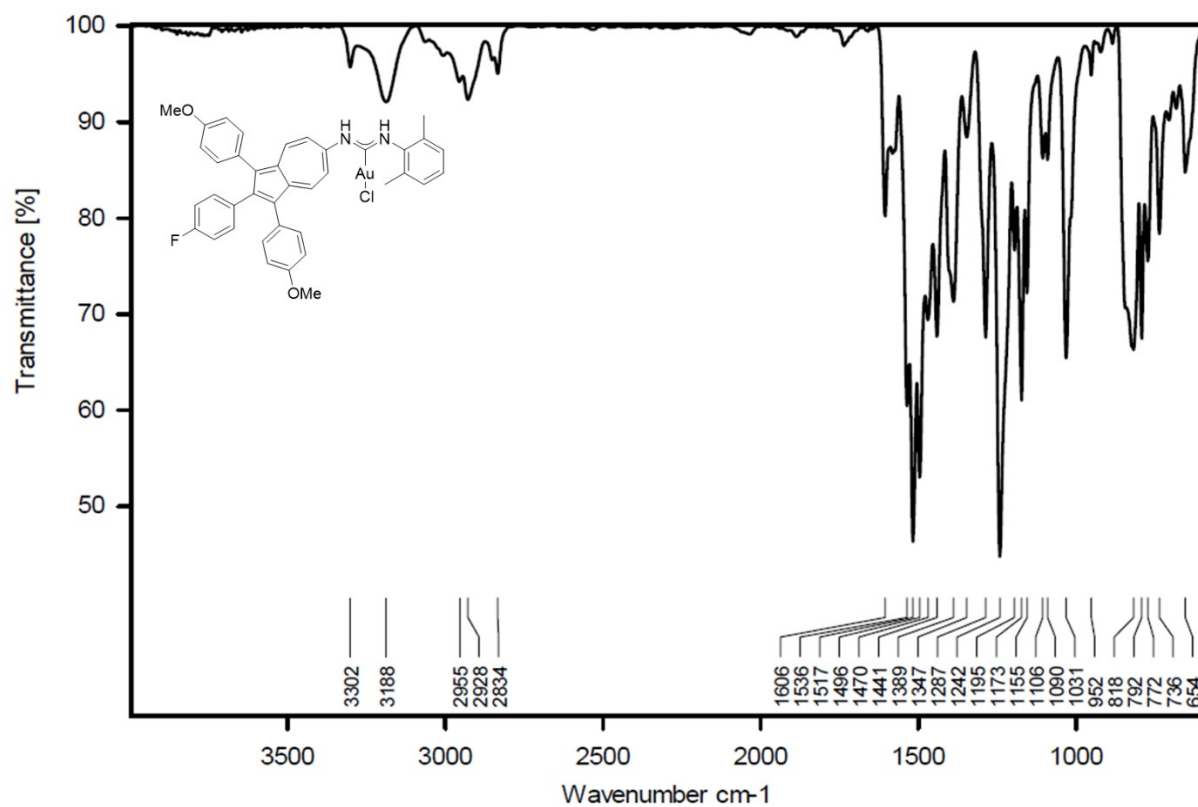


Figure S109. IR (ATR) Spectrum of **14bd**.

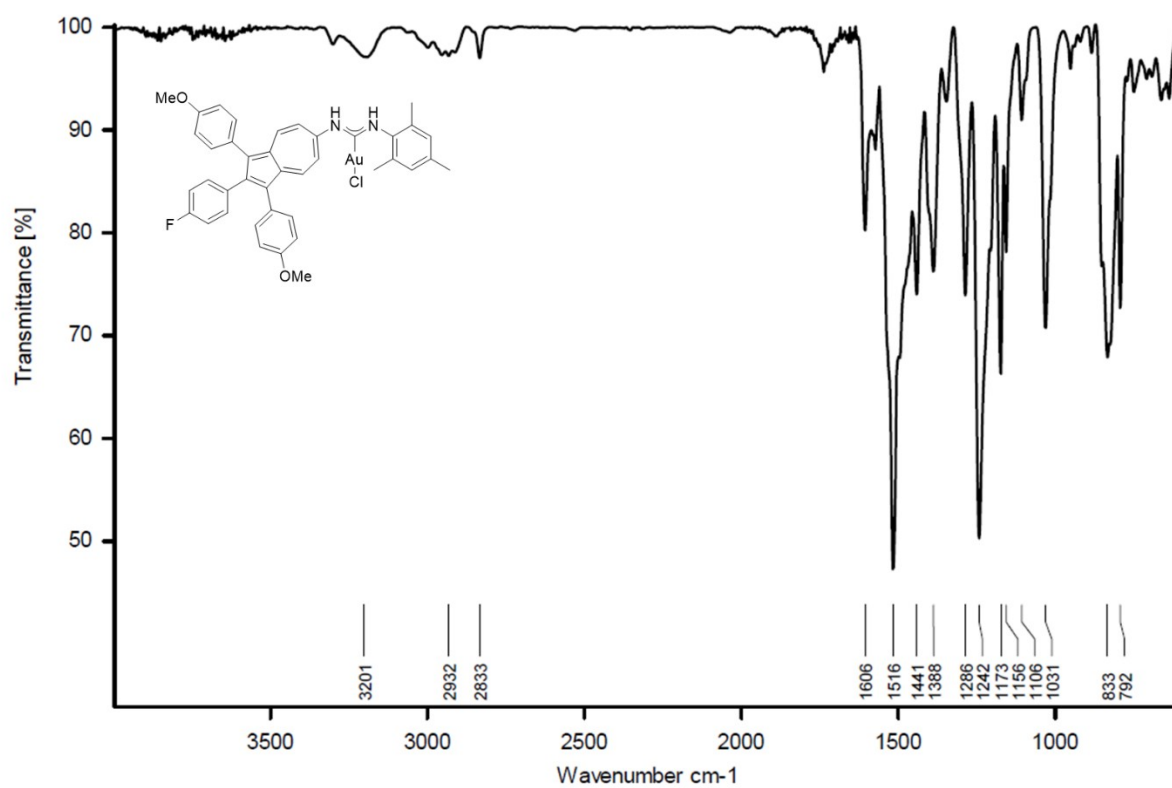


Figure S110. IR (ATR) Spectrum of **14be**.

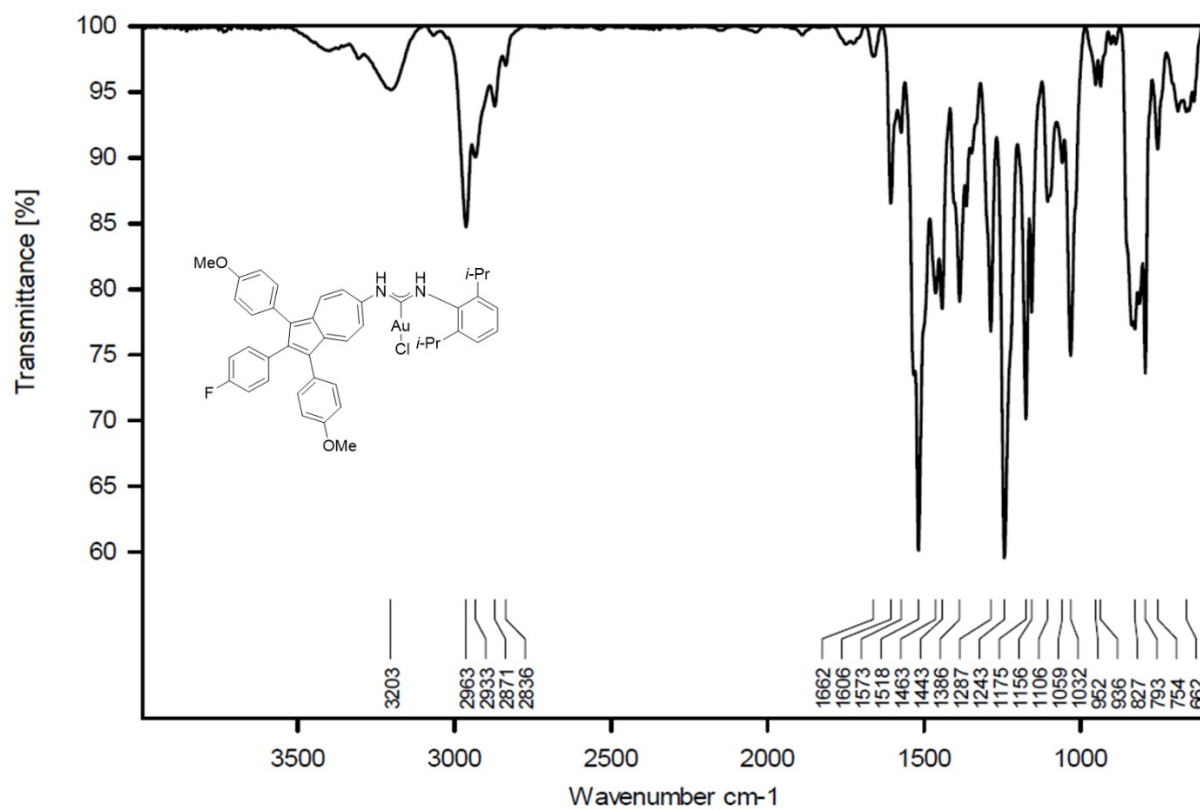


Figure S111. IR (ATR) Spectrum of 14bf.

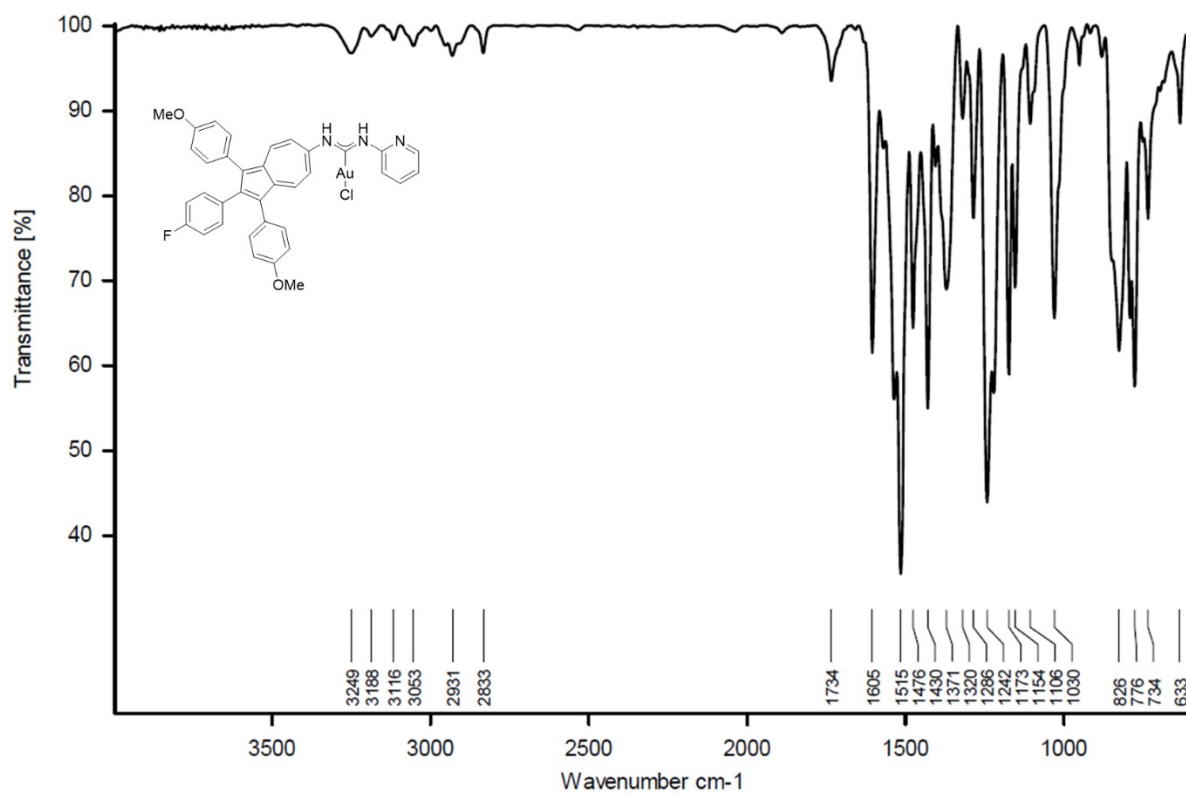


Figure S112. IR (ATR) Spectrum of 14bg.

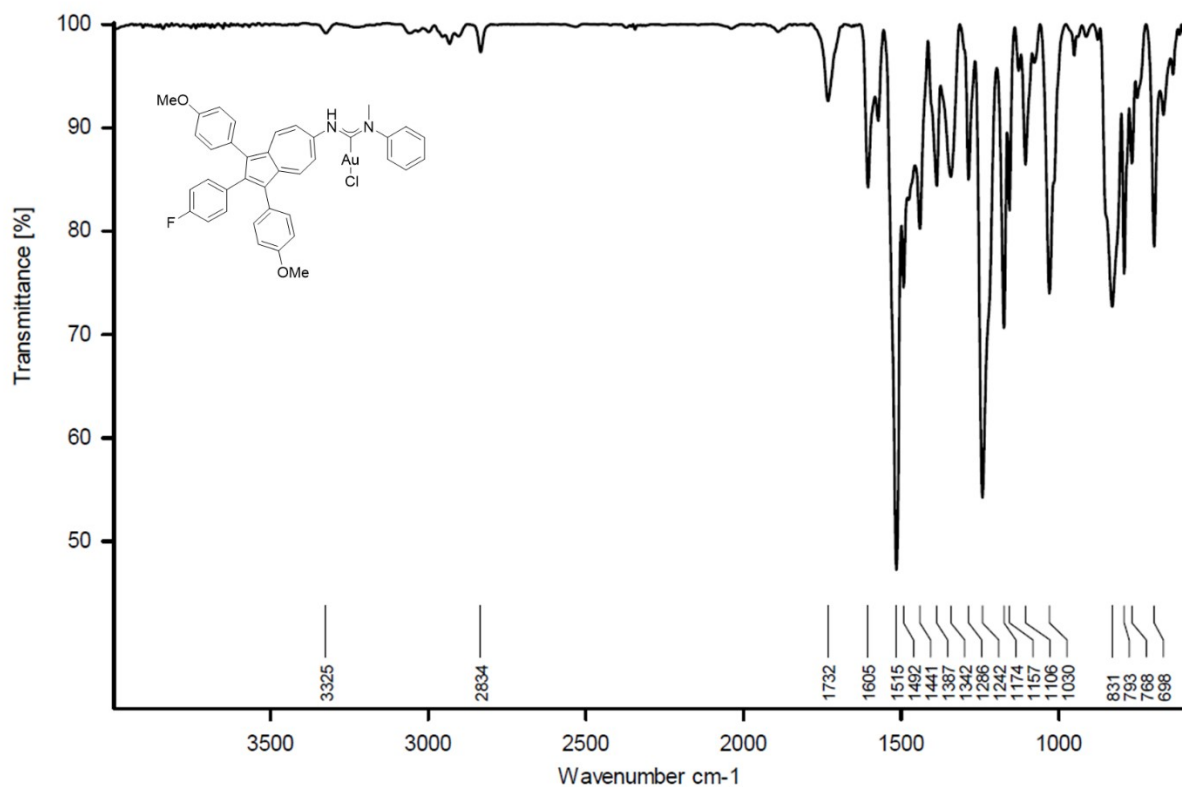


Figure S113. IR (ATR) Spectrum of **14bh**.

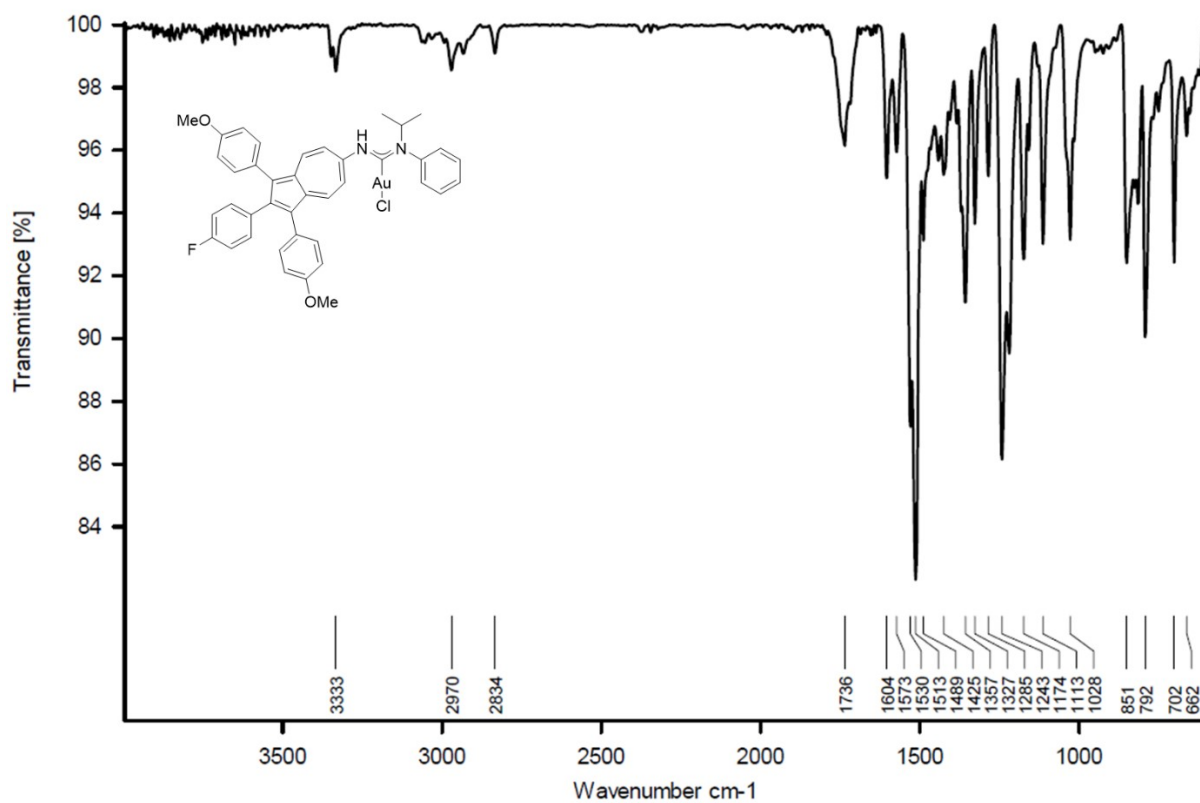


Figure S114. IR (ATR) Spectrum of **14bi**.

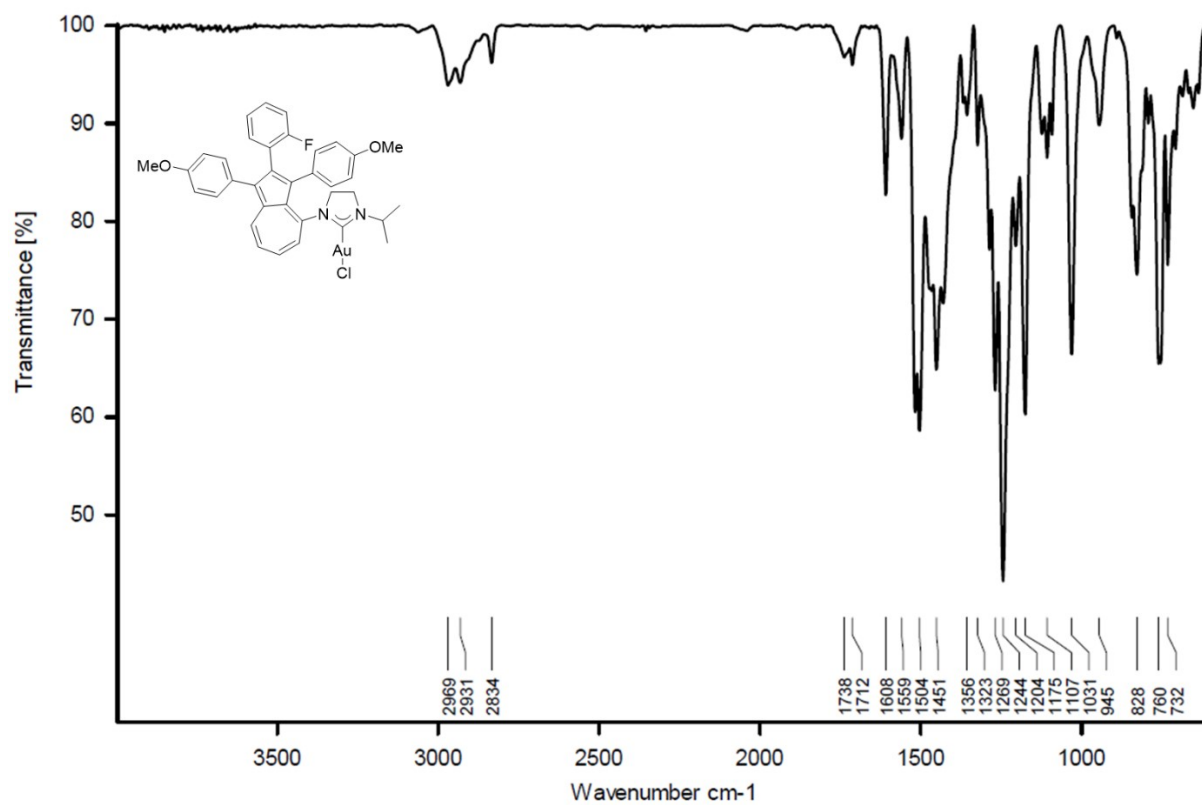


Figure S115. IR (ATR) Spectrum of 16a.

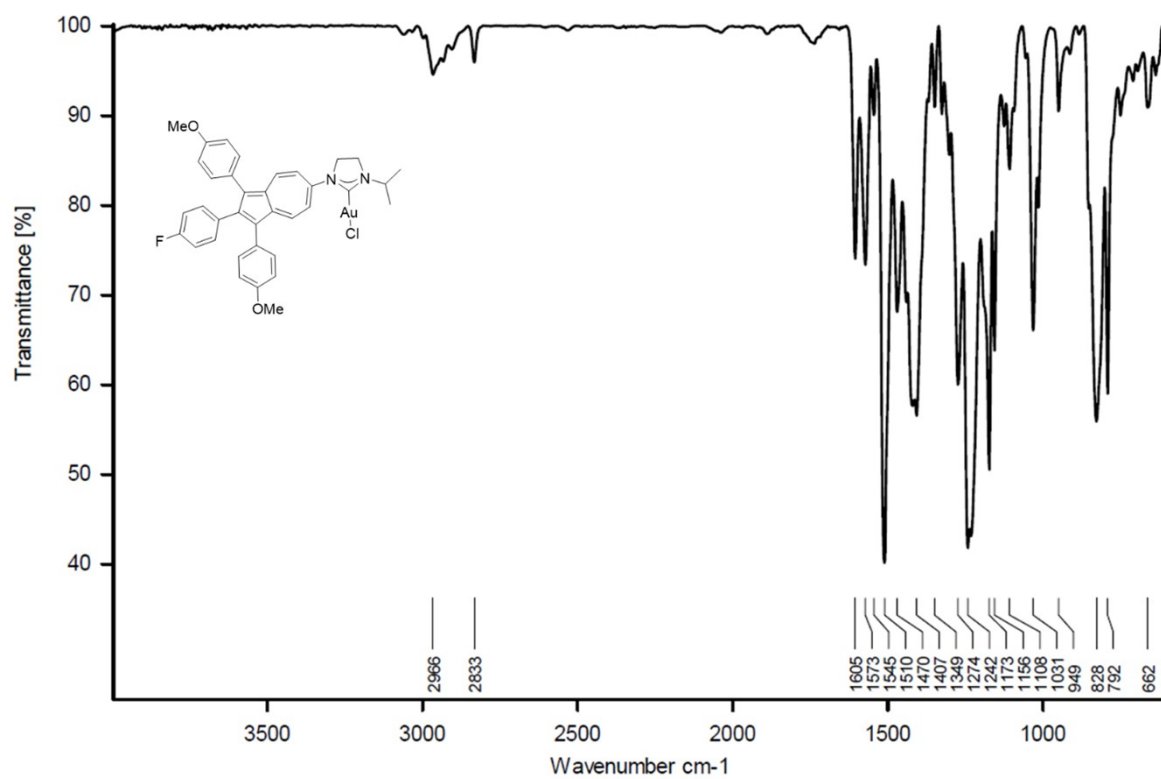
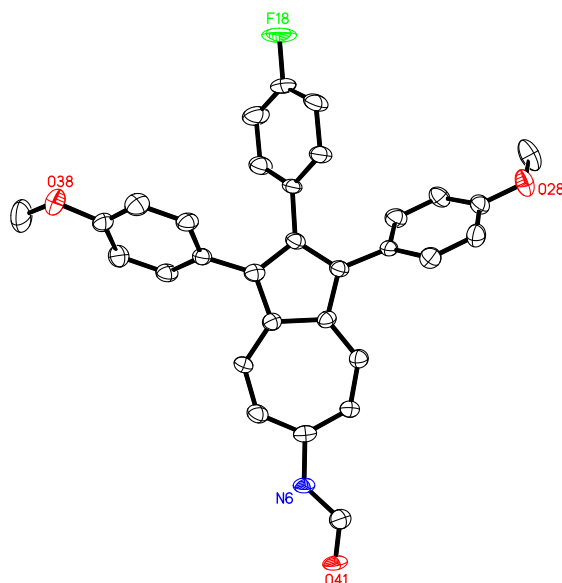


Figure S116. IR (ATR) Spectrum of 16b.

6 Single Crystal Structures

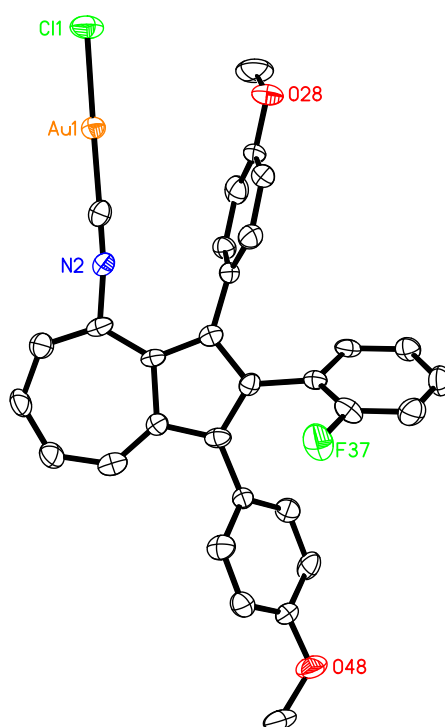
6.1 Single Crystal Structure of 6b

Identification code	mad3
Empirical formula	C ₃₃ H ₂₆ Cl ₆ FNO ₃
Formula weight	716.25
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	C2/c
Z	8
Unit cell dimensions	a = 23.3655(7) Å α = 90 deg. b = 9.5263(3) Å β = 108.2397(19) deg. c = 30.8642(10) Å γ = 90 deg.
Volume	6524.8(4) Å ³
Density (calculated)	1.46 g/cm ³
Absorption coefficient	0.57 mm ⁻¹
Crystal shape	plank
Crystal size	0.101 x 0.069 x 0.020 mm ³
Crystal colour	green
Theta range for data collection	1.4 to 22.7 deg.
Index ranges	-25 ≤ h ≤ 25, -10 ≤ k ≤ 10, -33 ≤ l ≤ 33
Reflections collected	32400
Independent reflections	4405 (R(int) = 0.0902)
Observed reflections	2853 (I > 2σ(I))
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.96 and 0.90
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	4405 / 0 / 399
Goodness-of-fit on F ²	1.03
Final R indices (I > 2σ(I))	R1 = 0.080, wR2 = 0.207
Largest diff. peak and hole	0.93 and -0.76 eÅ ⁻³



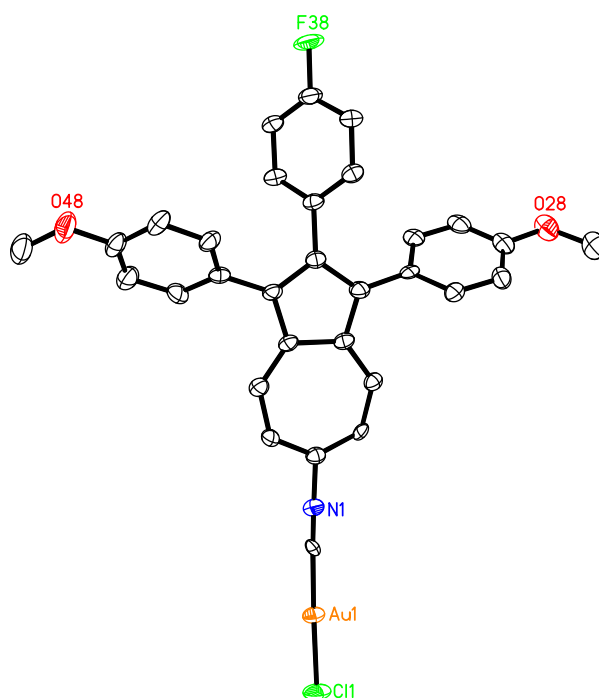
6.2 Single Crystal Structure of 10a

Identification code	mad2
Empirical formula	C ₃₁ H ₂₂ AuClFNO ₂
Formula weight	691.91
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	P2 ₁ /c
Z	4
Unit cell dimensions	a = 12.9318(6) Å α = 90 deg. b = 13.3667(6) Å β = 110.4578(12) deg. c = 15.7531(7) Å γ = 90 deg.
Volume	2551.3(2) Å ³
Density (calculated)	1.80 g/cm ³
Absorption coefficient	5.91 mm ⁻¹
Crystal shape	stick
Crystal size	0.078 x 0.035 x 0.026 mm ³
Crystal colour	green
Theta range for data collection	1.7 to 25.1 deg.
Index ranges	-15 ≤ h ≤ 15, -15 ≤ k ≤ 15, -18 ≤ l ≤ 18
Reflections collected	39986
Independent reflections	4513 (R(int) = 0.1145)
Observed reflections	3213 (I > 2σ(I))
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.89 and 0.75
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	4513 / 0 / 336
Goodness-of-fit on F ²	1.03
Final R indices (I > 2σ(I))	R1 = 0.037, wR2 = 0.061
Largest diff. peak and hole	1.01 and -0.75 eÅ ⁻³



6.3 Single Crystal Structure of 10b

Identification code	mad1	
Empirical formula	C ₃₂ H ₂₄ AuCl ₃ FNO ₂	
Formula weight	776.84	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P2 ₁ /n	
Z	12	
Unit cell dimensions	a = 7.0291(7) Å	α = 90 deg.
	b = 31.375(3) Å	β = 91.392(3) deg.
	c = 40.124(4) Å	γ = 90 deg.
Volume	8846.3(15) Å ³	
Density (calculated)	1.75 g/cm ³	
Absorption coefficient	5.30 mm ⁻¹	
Crystal shape	needle	
Crystal size	0.367 x 0.154 x 0.025 mm ³	
Crystal colour	green	
Theta range for data collection	1.0 to 23.3 deg.	
Index ranges	-7 ≤ h ≤ 7, -34 ≤ k ≤ 34, -44 ≤ l ≤ 44	
Reflections collected	68236	
Independent reflections	12691 (R(int) = 0.1642)	
Observed reflections	8164 (I > 2σ(I))	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.68 and 0.46	
Refinement method	Full-matrix least-squares on F ²	
Data/restraints/parameters	12691 / 2613 / 1087	
Goodness-of-fit on F ²	1.10	
Final R indices (I > 2σ(I))	R1 = 0.077, wR2 = 0.138	
Largest diff. peak and hole	1.58 and -1.90 eÅ ⁻³	

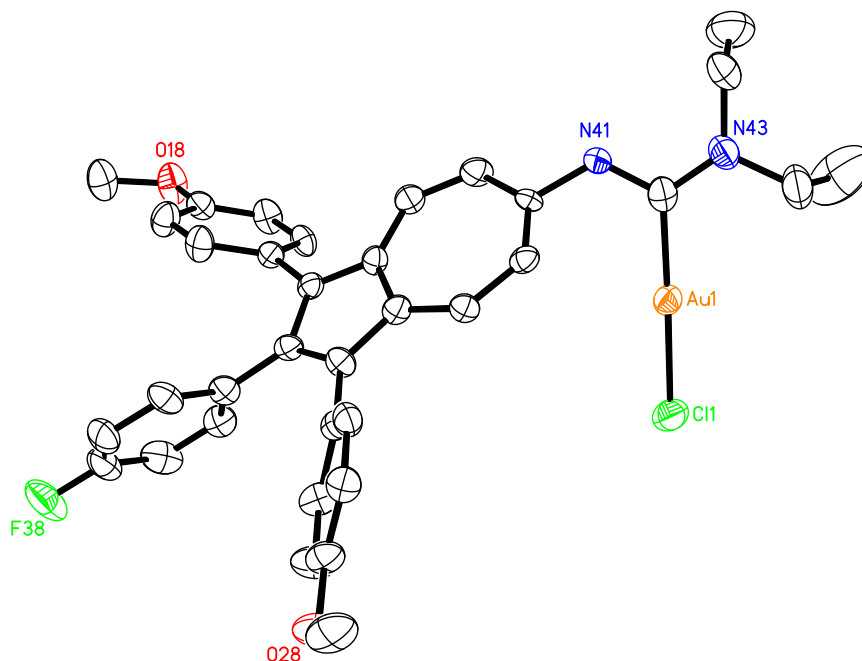


6.4 Single Crystal Structure of 14aa

Identification code	mad6
Empirical formula	C _{35.50} H ₃₄ AuCl ₂ FN ₂ O ₂
Formula weight	807.51
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system	tetragonal
Space group	P4 ₃ 2 ₁ 2
Z	8
Unit cell dimensions	a = 9.5430(2) Å α = 90 deg. b = 9.5430(2) Å β = 90 deg. c = 70.4724(16) Å γ = 90 deg.
Volume	6417.8(3) Å ³
Density (calculated)	1.67 g/cm ³
Absorption coefficient	4.79 mm ⁻¹
Crystal shape	plate
Crystal size	0.117 x 0.049 x 0.022 mm ³
Crystal colour	blue
Theta range for data collection	1.2 to 27.4 deg.
Index ranges	-12 ≤ h ≤ 12, -12 ≤ k ≤ 12, -91 ≤ l ≤ 91
Reflections collected	67172
Independent reflections	7332 (R(int) = 0.0829)
Observed reflections	6551 (I > 2σ(I))
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.91 and 0.78
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	7332 / 1 / 410
Goodness-of-fit on F ²	1.23
Final R indices (I > 2σ(I))	R1 = 0.039, wR2 = 0.085
Absolute structure parameter	0.019(4)

Largest diff. peak and hole

0.79 and -1.84 eÅ⁻³

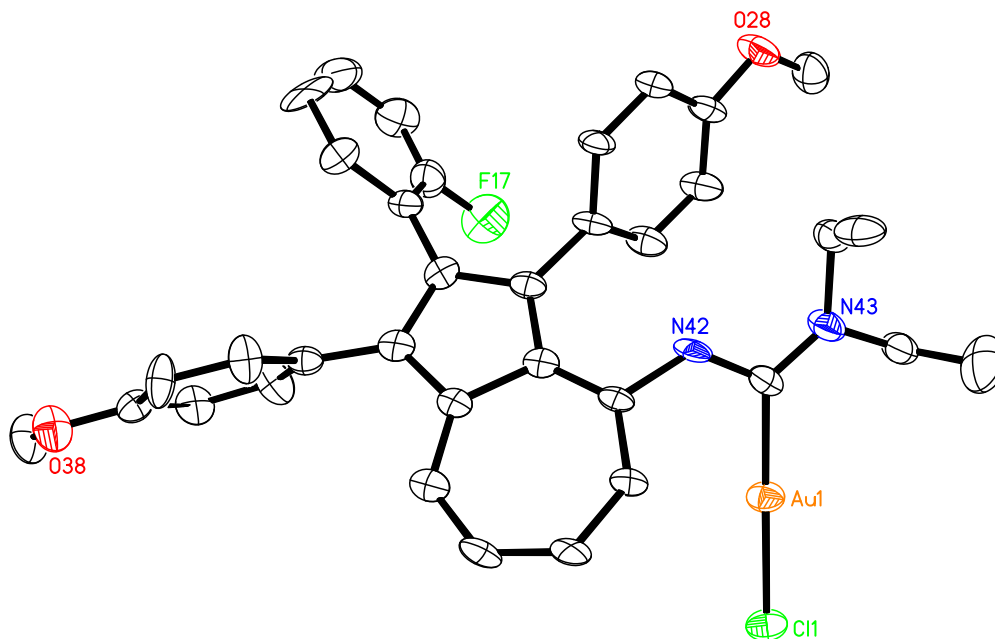


6.5 Single Crystal Structure of 14ba

Identification code	mad4	
Empirical formula	C ₃₅ H ₃₃ AuClFN ₂ O ₂	
Formula weight	765.05	
Temperature	102(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P2 ₁ /c	
Z	4	
Unit cell dimensions	a = 14.262(2) Å	α = 90 deg.
	b = 17.540(2) Å	β = 107.296(6) deg.
	c = 12.714(2) Å	γ = 90 deg.
Volume	3036.7(8) Å ³	
Density (calculated)	1.67 g/cm ³	
Absorption coefficient	4.97 mm ⁻¹	
Crystal shape	plank	
Crystal size	0.103 x 0.094 x 0.064 mm ³	
Crystal colour	blue	
Theta range for data collection	1.5 to 22.8 deg.	
Index ranges	-15 ≤ h ≤ 15, -18 ≤ k ≤ 19, -13 ≤ l ≤ 13	
Reflections collected	14410	
Independent reflections	4097 (R(int) = 0.1380)	
Observed reflections	2470 (I > 2σ(I))	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.91 and 0.64	
Refinement method	Full-matrix least-squares on F ²	
Data/restraints/parameters	4097 / 582 / 383	
Goodness-of-fit on F ²	1.01	
Final R indices (I > 2σ(I))	R1 = 0.057, wR2 = 0.113	

Largest diff. peak and hole

1.63 and -1.15 eÅ⁻³



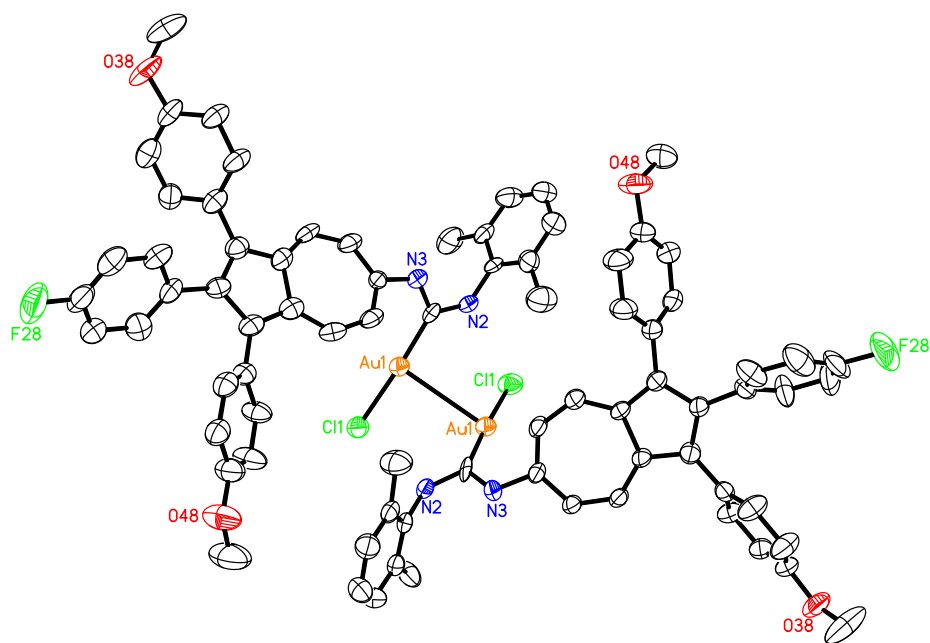
6.6 Single Crystal Structure of 14bd

Identification code	mad22
Empirical formula	C _{40.50} H _{34.50} AuClFN ₂ O ₂
Formula weight	832.62
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	P $\bar{1}$
Z	4
Unit cell dimensions	$a = 14.660(2)$ Å $\alpha = 89.298(3)$ deg. $b = 15.507(2)$ Å $\beta = 89.610(3)$ deg. $c = 15.652(2)$ Å $\gamma = 88.852(4)$ deg.
Volume	3557.2(8) Å ³
Density (calculated)	1.55 g/cm ³
Absorption coefficient	4.25 mm ⁻¹
Crystal shape	plank
Crystal size	0.075 x 0.025 x 0.015 mm ³
Crystal colour	blue
Theta range for data collection	1.3 to 20.5 deg.
Index ranges	-14 ≤ h ≤ 14, -15 ≤ k ≤ 15, -15 ≤ l ≤ 15
Reflections collected	29217
Independent reflections	7134 (R(int) = 0.0981)
Observed reflections	4723 (I > 2σ(I))
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.94 and 0.75
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	7134 / 1173 / 849
Goodness-of-fit on F ²	1.04
Final R indices (I > 2σ(I))	R1 = 0.055, wR2 = 0.127

S108

Largest diff. peak and hole

1.83 and -1.42 eÅ⁻³



7 IC₅₀ plots for complex 14aa

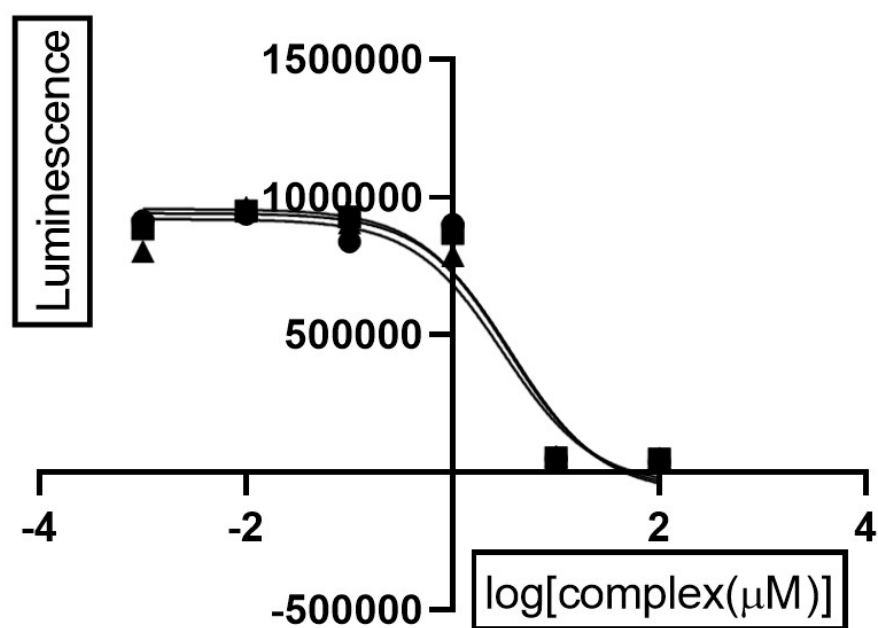


Figure S117. Plot for A2780.

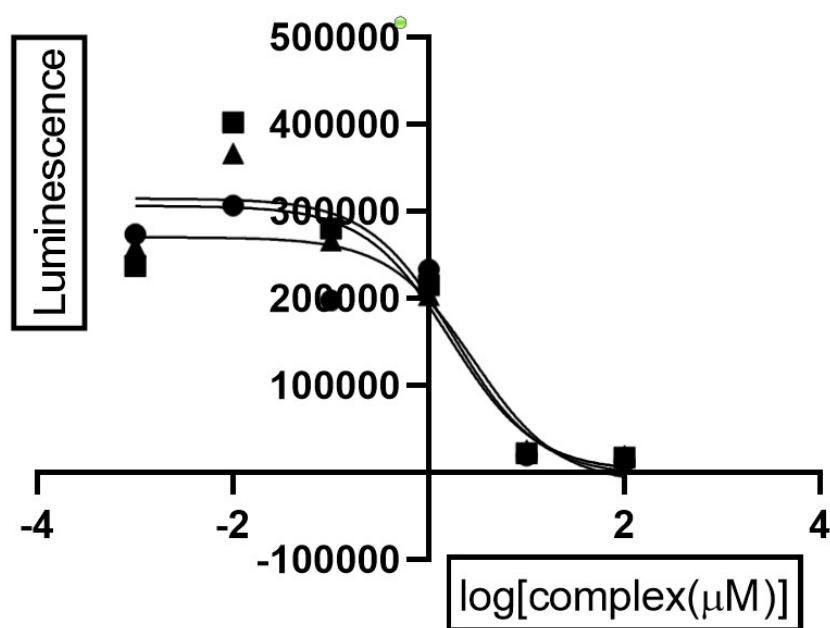


Figure S118. Plot for A2780cis.

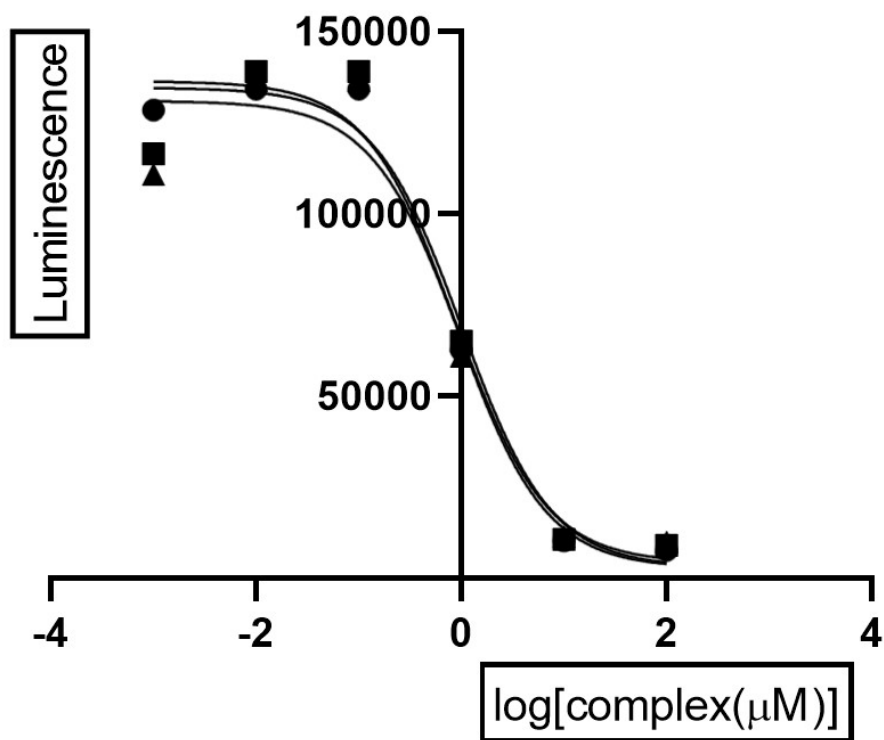


Figure S119. Plot for MDA-MB-231.

U87

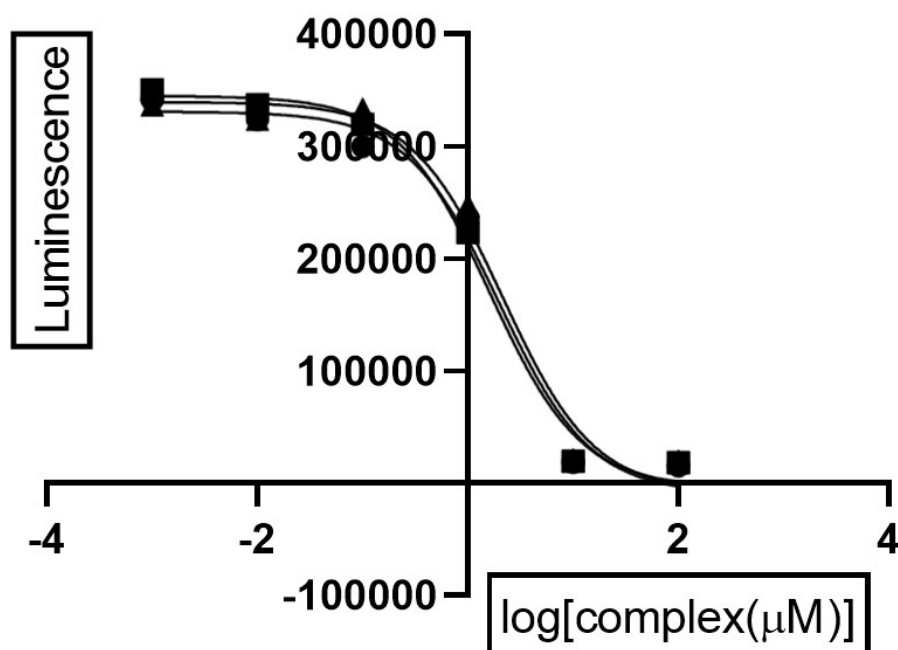


Figure S120. Plot for U87.

8 Stability of complexes **14ab** and **14ba**

To assess the stability of the used complexes in solution for the antiproliferative studies, exemplarily complexes **14ab** and **14ba** were dissolved in a 100 mM saline solution in D₂O and DMSO-d₆ in the ratio 1:5 and were left to stand at room temperature. ¹H NMR spectra of the solution were measured after t = 0 h, 24 h, 48 h, 72 h and 96 h. No decomposition was observed.

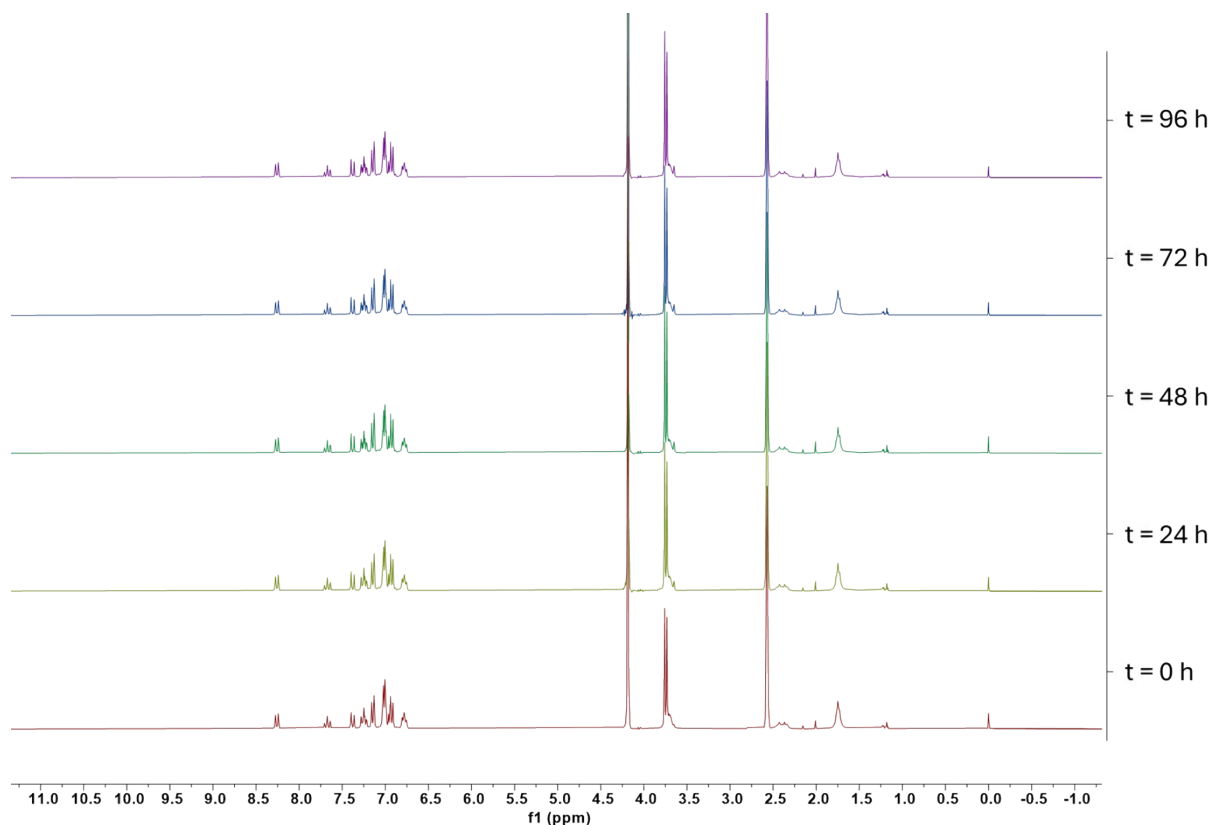


Figure S121. ¹H NMR Spectra (300 MHz, DMSO-d₆, 300 K) of **14ab** over the course of 96 h.

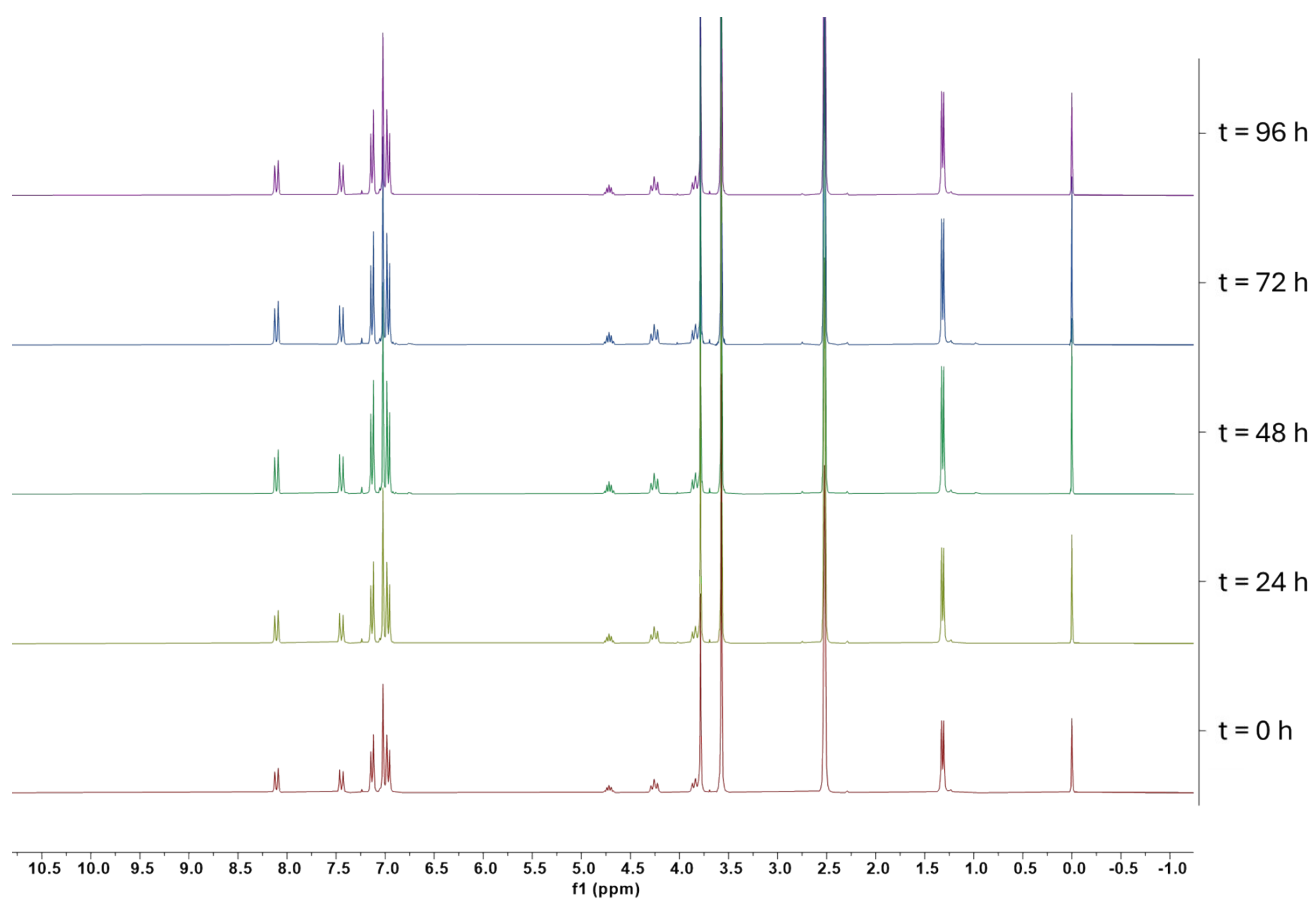


Figure S122. ^1H NMR Spectra (300 MHz, DMSO-d_6 , 300 K) of **14ba** over the course of 96 h.

9 References

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