3,5-Bis(3,5-bis(trifluoromethyl)phenyl)pyrazolyl complexes of Coinage Metals

by

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ABSTRACT

3,5-BIS(3,5-BIS(TRIFLUOROMETHYL)PHENYL) PYRAZOLYL COMPLEXES OF COINAGE METALS

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Pyrazole is an important class of five membered heterocyclic compound consisting of two nitrogen atoms. Pyrazolate anions serve as useful ligands in coordination chemistry. When fluorinated substituents are attached to this ligand they provide favorable properties such as volatility, thermal and oxidative stability. Trinuclear pyrazolate complexes of monovalent coinage metals (i.e., Cu(I), Ag(I), and Au(I)) represent an important class of compounds with interesting structures and fascinating properties. Little has been done in adding sterically hindered substituents onto the pyrazole ring. This thesis includes the introduction of heavily fluorinated bulky aryl substituents such as 3,5-$(CF_3)_2$Ph- at the 3- and 5- position of the pyrazole ring resulting in the synthesis of [3,5-(3,5-$(CF_3)_2$Ph$)_2$PzH] as a novel pyrazole. The trinuclear metal pyrazolate complexes of monovalent coinage metals like Cu(I), Ag(I), and Au(I) of this pyrazole were also synthesized and it was found that the metal complexes of this pyrazole showed luminescence properties as were exhibited by most of the previously reported metal pyrazolate complexes. The frozen solutions of metal complexes of this pyrazolate shows bright luminescence upon exposure to UV radiation. The frozen solutions of $\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]Cu\}_3$ and $\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]Ag\}_3$ complex showed light green

colored emission at 77 K whereas $\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]Au\}_3$ showed bright blue colored emission when irradiated under long wavelength UV radiation (366 nm). Due to the bright luminescence of $\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]Au\}_3$, it may serve as a promising candidate for light emitting device applications.

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List of Abbreviations

NaH	Sodium hydride
$[3,5-(3,5-(CF_3)_2Ph)_2Pz]H$	3,5-bis(3,5-bis(trifluoromethyl)phenyl)-1H-pyrazole
$\{[3,5-(3,5-(CF_3)_2Ph)_2Pz]Ag\}_3$	Trinuclear silver (I) complex of $[3,5-(3,5-(CF_3)_2Ph)_2Pz]$
$\{[3,5-(3,5-(CF_3)_2Ph)_2Pz]Au\}_3$	Trinuclear gold (I) complex of $[3,5-(3,5-(CF_3)_2Ph)_2Pz]$
$\{[3,5-(3,5-(CF_3)_2Ph)_2Pz]Cu\}_3$	Trinuclear copper (I) complex of $[3,5-(3,5-(CF_3)_2Ph)_2Pz]$
Ag	Silver
Ag_2O	Silver(I)oxide
Au	Gold
Au(THT)Cl	Chloro(tetrahydrothiophene)gold(I)
$CDCl_3$	Deuterated chloroform
CH_3	Methyl
CH_3OH	Methanol
Cu	Copper
$Cu(CH_3CN)_4 . BF_4$	Tetrakisacetonitilecopper(I)tetrafluoroborate
DI	De-Ionized
Et_2O	Diethyl ether
H_2	Hydrogen gas
HCl	Hydrochloric acid
I.R	Infrared
N_2	Nitrogen gas
$NaBF_4$	Sodium tetrafluoroborate
NMR	Nuclear Magnetic Resonance
Ph	Phenyl

Pz	Pyrazole
RBF	Round bottom flask
RT	Room temperature
THF	Tetrahydrofuran
TLC	Thin layer chromatography
UV	Ultraviolet

CHAPTER 1

3,5-BIS(3,5-BIS(TRIFLUOROMETHYL)PHENYL) PYRAZOLYL COMPLEXES OF COINAGE METALS

Introduction

The coordination chemistry of d-10 transition metal pyrazolates is of significant interest. The basic structural unit of these metal pyrazolate complexes is a pyrazole. Pyrazoles, are aromatic heterocycle containing two nitrogen atoms in their five-membered rings. (**Figure 1**). The pyrazole nucleus is fairly stable.[1] When deprotonated, the pyrazole becomes pyrazolate ion which can coordinate to metal atoms as an anionic ligand.

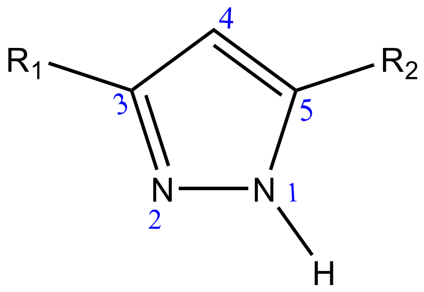

Figure 1. Five membered ring structure of pyrazole.

The pyrazolate anion is known to exhibit three coordination modes on binding to metal centers (**Figure 2**). [2–4] It can act as an anionic monodentate, an anionic *endo*-bidentate or an anionic *exo*-bidentate ligand (**Figure 2**; b, c, d, respectively).[5-11] In this present study, the co-ordination of coinage metal ions (i.e. **M** = Cu, Ag and Au) to pyrazolate in an exo-bidentate mode is observed.

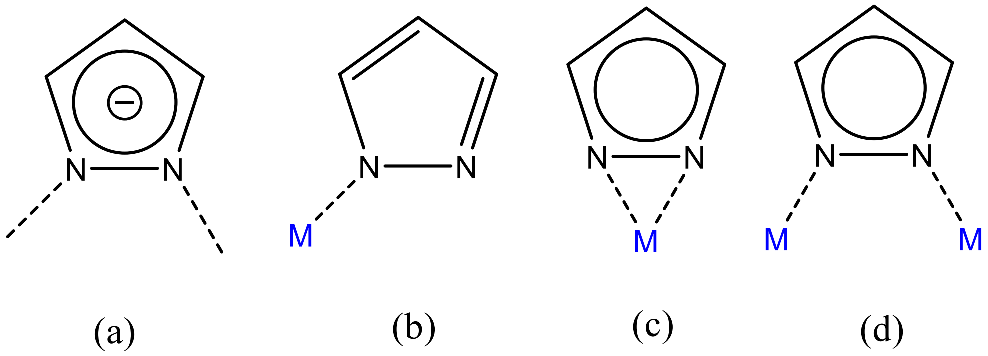

Figure 2. Pyrazolate anion and co-ordination modes.

Metal-metal and metal-ligand interaction in coinage metal pyrazolates promotes luminescence properties[12-19] and hence such metal pyrazolate complexes are attractive candidates for emitting materials in molecular light-emitting device applications[20], semiconductors and liquid crystals.[21] The frozen solutions of some of the complexes of these coinage metal pyrazolates exhibit different colors with different temperature, solvent and at different excitation wavelengths.[22] The properties of these pyrazolate complexes can be altered by substitution at position 3 and 5 of pyrazole ring. Presence of electronegative species at position 3 and 5 result in the π-acidic nature whereas electron rich species promote the nucleophilic nature of the pyrazolate complex.[23-25] Various electron withdrawing fluorinated substituents at position 3 and 5 of the pyrazolyl rings have been attempted so far to enhance acidic nature of the pyrazole[26-40] as listed in Table 1. Among the electron withdrawing substituents, highly fluorinated phenyl groups have not been explored based on the survey of current literature.

This study involves the use of such phenyl substituents on the pyrazole ring structure. As evident from the data presented in this work, the metal pyrazolate complexes of these highly fluorinated phenyl substituents on the pyrazole moiety resulted in a steric environment such that the corresponding trinuclear metal pyrazolate complexes are not planar in the solid state. These complexes also exhibit luminescence properties as depicted by other previously reported coinage metal pyrazolate complexes and are potential candidates for catalysis.

Table 1: Reported Pyrazoles with fluorinated substitutions.[26-40]

<table>
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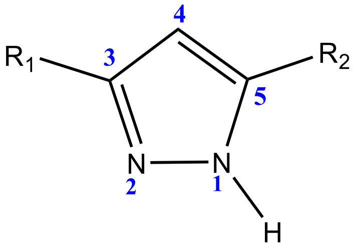 </td></tr>
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</table>

Results and Discussion

1,3-bis(3,5-bis(trifluoromethyl)phenyl)-3-hydroxyprop-2-en-1-one

The diketone 1,3-bis(3,5-bis(trifluoromethyl)phenyl)-3-hydroxyprop-2-en-1-one, was synthesized by the reaction of a mixture of 3,5-bis(trifluoromethylbenzoate and 3,5-bis(trifluoromethyl)acetophenone under basic condition using modified literature method[41] used for the synthesis of 1,3-bis(4-methylphenyl)propane-1,3-dione.

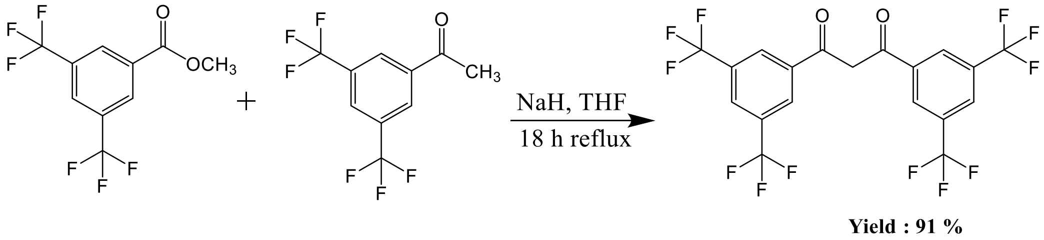

Figure 3. Synthesis of 1,3-bis(3,5-bis(trifluoromethyl)phenyl)-3-hydroxyprop-2-en-1-one.

The reaction resulted in better yield of 91% when the two reactants were added at the same time into reaction mixture as a solution in THF under cold condition as compared to when reactants are added one after another. Firstly, deprotonation of CH_3 group of bis(trifluoromethyl)acetophenone takes place along with removal of H_2 gas from the reaction mixture. This step is followed by a nucleophilic attack on 3,5-bis(trifluoromethylbenzoate resulting in the elimination of CH_3OH and formation of diketone. The reaction progress was monitored by Thin Layer Chromatography on silica TLC plate. Disappearance of reactant spots on TLC plate was used as a basis for reaction completion. The diketone is soluble in chloroform, tetrahydrofuran, and acetone with higher solubility in acetone and tetrahydrofuran. The retention factor for diketone was found to be 0.88 on acetone/hexane (2:3). The melting point of the diketone crystals was found to be 173 ^{0}C and the diketone started decomposing at temperature above 200 ^{0}C. The Infra-red Spectrum of the diketone showed peaks at 909 cm^{-1},1114 cm^{-1}, 1148 cm^{-1}which corresponds to C-F, and C-O stretching vibration frequencies, respectively and, 1366 cm^{-1} corresponds to C-H bending vibrational frequency.**[31]**

The ^{1}H spectra of the diketone shows a peak corresponding to four C-H protons on the aromatic rings at 8.43 ppm whereas other two C-H protons on the aromatic rings appear at 8.10 ppm. The CH_2 proton appear at 6.89 ppm. The ^{19}F NMR shows a singlet at -62.74 ppm which proves that the diketone structure is symmetrical in nature. The ^{13}C NMR Spectrum of the diketone consists of a peak at 183.7 ppm which corresponds to carbon of C=O group. The C(7) appears at 137.2 ppm as a singlet. C(2,4) appears as a quartet at 133.4 ppm. The aromatic carbons C(10,6) appears as one peak at 127.7 ppm. C (1,5) appear at 126.5 ppm. C(3) appear at 124.3 ppm. C(9) appear at 94.2 ppm. The ^{1}H and ^{13}C NMR spectra suggest that the diketone undergo rapid keto-enol tautomerism in solution state.

3,5-(3,5-$(CF_3)_2$Ph)$_2$PzH

The pyrazole i.e. 3,5-(3,5-$(CF_3)_2$Ph)$_2$PzH, was synthesized by the slow addition of hydrazine hydrochloride solution in water to 3-bis(3,5-bis(trifluoromethyl)phenyl)-3-hydroxyprop-2-en-1-one solution in THF.

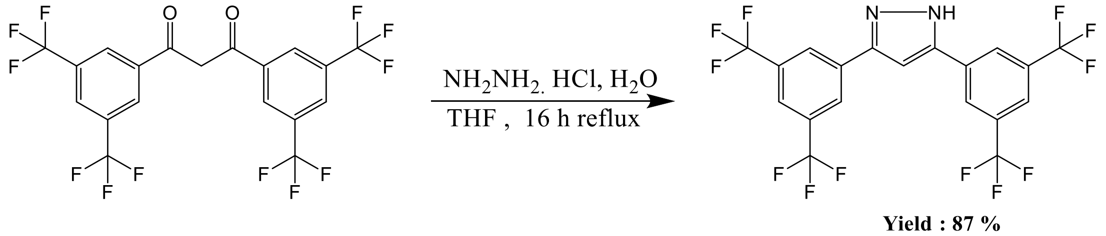

Figure 4. Synthesis of 3,5-(3,5-$(CF_3)_2$Ph)$_2$PzH.

An aldol condensation reaction takes place resulting in the formation of desired pyrazole and water is eliminated as a byproduct. The use of hydrazine hydrochloride instead of hydrazine hydrate resulted in better product formation. So, the reaction occurs in presence of catalytic amount of hydrochloric acid. When the reaction is complete, the reaction mixture was neutralized by the addition of ice cold water to precipitate the product. The reaction yielded 87% of the pyrazole. The melting point of pyrazole was found to be 188-190^{0}C and it started decomposing above 235^0 C. To obtain dry pyrazole, the sublimation of crude pyrazole was performed at around 175^0 C under vacuum. Sublimation was time consuming, so the product was purified by crystallization. The pyrazole was crystallized from hot chloroform as cubic sugar like crystals. From the crystal structure, it was found that the pyrazole crystallized as a trimer indicating that making trinuclear metal complexes of pyrazole is feasible.

The pyrazole is soluble in acetone and tetrahydrofuran at room temperature and soluble in benzene and chloroform at a higher temperature. The retention factor for pyrazole was found to be 0.76 on acetone/hexane (2:3). The IR Spectrum for the pyrazole showed peaks at 890 cm-^{1}, 1126 cm^{-1}, 1171 cm^{-1} and 1282 cm^{-1} which corresponds to C-F, C-O and C-N stretching vibration frequency respectively and, 1359 cm^{-1} corresponds to C-H bending vibrational frequency.**[42]**

The ^{1}H NMR Spectrum includes three peaks. They can be assigned as 8.19 ppm due to four aromatic CH, at 7.90 ppm due to two aromatic CH, and at 7.11 ppm due to CH of the pyrazole ring.

^{19}F NMR Spectrum shows a singlet at -62.86 ppm indicating pyrazole to be symmetrical in solution on NMR time scale.

The ^{13}C NMR Spectrum of the pyrazole (**Figure 5**) consists of a peak at 102.5 ppm which corresponds to C(1). The aromatic C-H carbon C(7) appears at 119 ppm as a singlet. CF_3 carbons C(10, 6) of CF_3 groups appear at 121. ppm and 121.8 ppm. The aromatic carbons C(9, 4) appear at 125.4ppm and 125.6ppm . C(5,8) appear at 129.4 ppm. C(3) appear at 131.7 ppm. C(2) appear at 131.9 ppm.

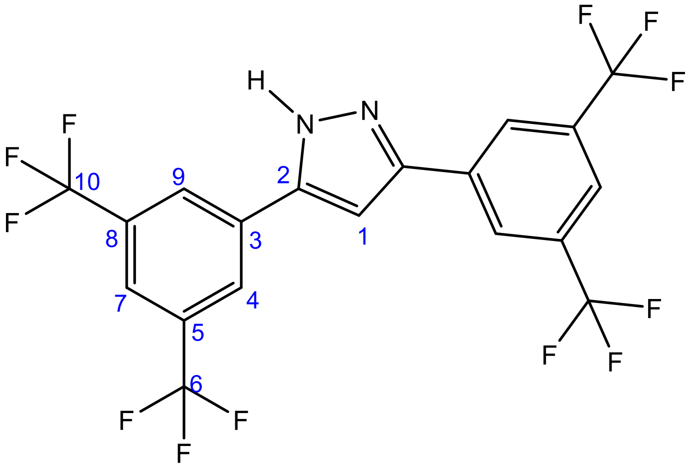

Figure 5. 3,5-(3,5-$(CF_3)_2$Ph$)_2$PzH.

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{[3,5-(3,5-$(CF_3)_2$Ph)$_2$Pz]Cu}$_3$

The trinuclear pyrazolate complex of copper was synthesized using $Cu(CH_3CN)_4BF_4$ as the copper precursor. $Cu(CH_3CN)_4BF_4$ was synthesized using copper(I) oxide in CH_3CN by a literature method**[43]**. $Cu(CH_3CN)_4BF_4$ was stored under an inert atmosphere and was protected from light using aluminum foil as this complex decomposes in open air. The synthesis of the trinuclear pyrazolate complex of copper involves the deprotonation of pyrazole using NaH followed by the slow addition of deprotonated pyrazole i.e. pyrazolate solution in THF to the copper(I) complex i.e. $Cu(CH_3CN)_4BF_4$ in THF at 0 ^{0}C. As the reaction reaches room temperature, after this addition, the reaction mixture turned slight green to pale yellow and then clear and after 30 minutes, the reaction mixture turned cloudy indicating the start of biproduct i.e. $NaBF_4$ generation. The reaction mixture was refluxed under nitrogen atmosphere and reaction progress was monitored by the chemical shift in ^{19}F NMR Spectrum of the reaction mixture. The reaction was complete in 3.6 days.

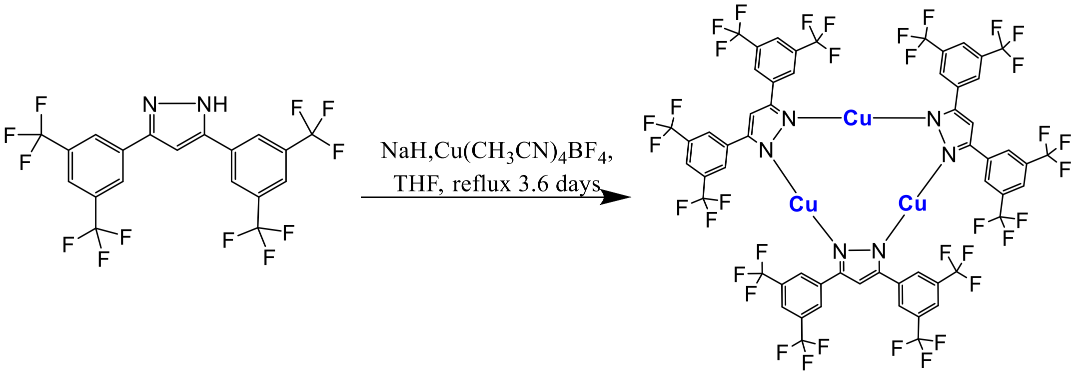


Figure 6. Synthesis of {[3,5-(3,5-$(CF_3)_2$Ph)$_2$Pz]Cu}$_3$

After the completion of reaction, the product was separated from the byproduct by filtration. A significant upfield shift in the ^{1}H and ^{19}F NMR signals of the product with respect to the starting material i.e. [3,5-(3,5-$(CF_3)_2$Ph)$_2$PzH confirmed the formation of {[3,5-(3,5-$(CF_3)_2$Ph)$_2$Pz]Cu}$_3$.The product was purified by recrystallization from toluene and it was found that some of the solvent i.e. toluene molecules got trapped in the copper trimer crystals and this could be easily visualized from the ^{1}H NMR spectrum of the crystals dried for one day under vacuum at 50 ^{0}C. Under the influence of long wavelength of UV light (366 nm) and at -78 ^{0}C, the product i.e. Cu-trimer emits light green light.

{[3,5-(3,5-(CF_3)$_2$Ph)$_2$Pz]Ag}$_3$

The trinuclear pyrazolate complex of silver(I), {[3,5-(3,5-(CF_3)$_2$Ph)$_2$Pz]Ag}$_3$, was synthesized using a literature method**[44]** similar to the synthesis of {[3-(CF_3)Pz]Ag}$_3$ by reacting pyrazole with excess silver (I) oxide

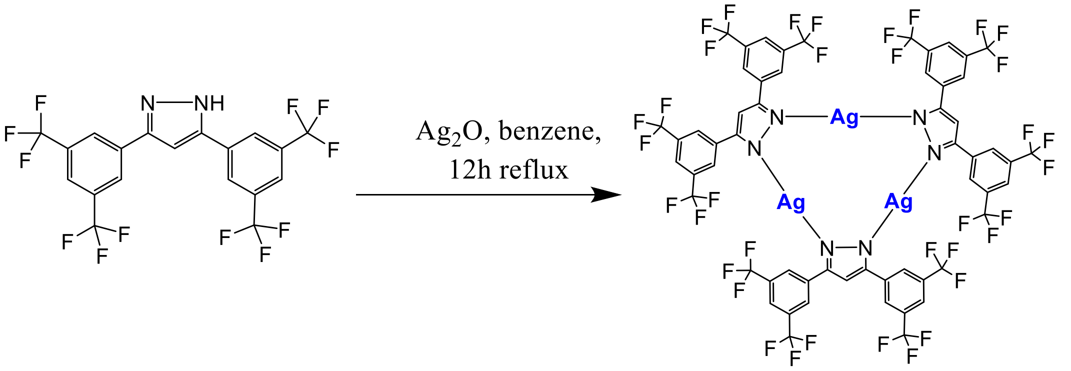


Figure 7. Synthesis of {[3,5-(3,5-(CF_3)$_2$Ph)$_2$Pz]Ag}$_3$

benzene was used as the solvent and the mixture was refluxed overnight. After the reaction is complete as indicated by the^{19}F NMR spectrum, the reaction mixture was filtered through a Celite bed to eliminate insoluble black material. The silver pyrazolate product is obtained in high yields (>80%). The product is readily soluble in most of the common organic solvents such benzene, dichloromethane, acetonitrile, toluene, and tetrahydrofuran and soluble in hot hexane. The product was recrystallized from dichloromethane. When crystallized from toluene, the product formed a toluene adduct which is evident from the ^{1}H NMR spectral data. A significant upfield shift in the ^{1}H and ^{19}F NMR signals of the product with respect to the starting material i.e. [3,5-(3,5-(CF_3)$_2$Ph)$_2$PzH confirmed the formation of {[3,5-(3,5-(CF_3)$_2$Ph)$_2$Pz]Ag}$_3$ .The product is light and moisture sensitive, so must be stored under nitrogen and protected from light. Under the influence of long wavelength of UV light and -78 ^{0}C, silver-trimer emits light green light.

{[3,5-(3,5-(CF$_3$)$_2$Ph)$_2$Pz]Au}$_3$

The trinuclear pyrazolate complex of gold was synthesized using Au(THT)Cl as a precursor for gold. Au(THT)Cl was synthesized using gold(III) chloride by a literature method[45]. Au(THT)Cl was stored under ice cold conditions and in an inert atmosphere as this complex readily decomposes at room temperature. The synthesis of the trinuclear pyrazolate complex of gold involves the deprotonation of pyrazole using NaH followed by the slow addition of deprotonated pyrazolate solution in THF to Au(THT)Cl in THF at 0 ^{0}C. After this addition, the mixture was brought to room temperature. It turned clear after 30 minutes, and then turned cloudy upon further stirring. The reaction progress was monitored by the ^{19}F NMR spectroscopy. The reaction was complete in 36 hours.

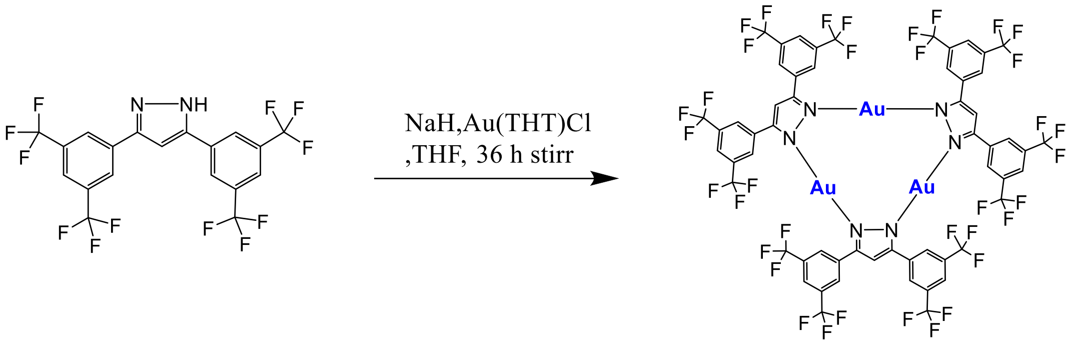


Figure 8. Synthesis of {[3,5-(3,5-(CF$_3$)$_2$Ph)$_2$Pz]Au}$_3$

After the completion of reaction, the product was separated from the byproduct by filtration. A significant upfield shift in the ^{1}H and ^{19}F NMR resonances of the product with respect to the starting material i.e. [3,5-(3,5-$(CF_3)_2$Ph)$_2$PzH confirmed the formation of {[3,5-(3,5-$(CF_3)_2$Ph)$_2$Pz]Au}$_3$. The product was purified by recrystallization from toluene. It was found to be light sensitive. For example, exposure to light for 2 days resulted in the conversion of the complex back to the starting pyrazole ligand. Under the influence of long wavelength of UV light (366 nm), this gold-trimer emits bright blue light. Its photophysical properties were studied and excitation and emission spectra were recorded (**Figure 9**). {[3,5-(3,5-$(CF_3)_2$Ph)$_2$Pz]Au}$_3$ exhibited bright blue luminescence with emission maxima near 480- 490 nm and stoke shift on the order of 2111 cm^{-1} (λ_{Exc} **=** 365 nm at RT).

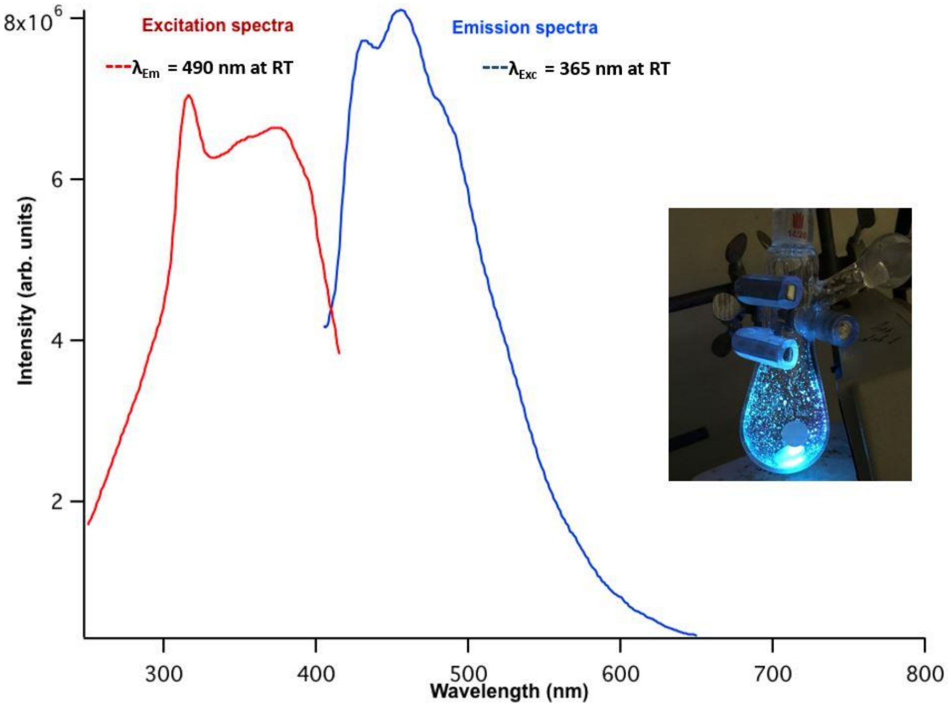


Figure 9. Emission and excitation spectra of a crystalline solid sample of {[3,5-(3,5-$(CF_3)_2$Ph)$_2$Pz]Au}$_3$ at RT . A photograph showing the emission color of solid {[3,5-(3,5-$(CF_3)_2$Ph)$_2$Pz]Au}$_3$ sample at RT under UV irradiation.

CHAPTER 2

EXPERIMENTAL DETAILS

General Procedures. All manipulations were carried out under an atmosphere of purified nitrogen using either standard Schlenk techniques or in a Vacuum Atmospheres single station dry box equipped with a -25 ^{0}C refrigerator. Solvents were purchased from commercial sources and distilled from conventional drying agents prior to use. Glassware was oven dried at 150 ^{0}C overnight. The NMR spectra were recorded at room temperature on a JEOL Eclipse 500 spectrometer (^{1}H, 500.16 MHz; ^{19}F, 470.62 MHz; ^{13}C, 125.78 MHz). Proton and carbon chemical shifts are reported in parts per million vs. Me_4Si. ^{19}F chemical shifts were referenced to external $CFCl_3$ standard. Infrared spectra were recorded on a JASCO FT-IR 410 spectrometer. Melting points were obtained on a Mel-Temp II apparatus. Elemental analyses were performed at the University of Texas at Arlington using a Perkin-Elmer Model 2400 CHN analyzer. The $Cu(CH_3CN)_4BF_4$ and Au(THT)Cl were synthesized as reported previously. Silver(I) oxide was purchased from Sigma Aldrich.

1,3-bis(3,5-bis(trifluoromethyl)phenyl)-3-hydroxyprop-2-en-1-one: NaH (0.35 g, 14.64 mmol, 60% in oil) was washed free from oil with dry hexane (10 mL) at 0ºC under N_2. Dry THF (5 mL) was added, followed by a mixture of 3,5-bis(trifluoromethylbenzoate (2.75 g, 10.74 mmol) and 3,5-bis(trifluoromethyl)acetophenone (2.5 g, 9.76 mmol) in dry THF (10 mL) at 0ºC under N_2. The suspension was stirred under reflux for 18 h. The mixture was cooled and filtered (Celite®). The solid was washed with EtOH (20 mL). The combined filtrates were poured into Et_2O (20 mL) and aq. HCl (1 M, 20 mL). The aq. layer was extracted (Et_2O, 2 ×). The combined extracts were washed (brine, 3 ×) and dried. The solvent was evaporated in vaccuo to get an orange solid which was washed many times with hexane to get white solid. (4.42 g, 91.3 %). The product was recrystallized from hot Chloroform/hexane (3:2) as colorless shiny prismatic flakes. mp 173 ºC; ^{1}H NMR ($CDCl_3$, 300 MHz) (enol) δ 16.58 (1 H, s, OH) 8.43 (4 H, s, ar CH), 8.10 (2 H, s, ar CH), 6.86 (1 H, s, CH_2). ^{19}F NMR -62.39 ppm. Anal. Calcd for $C_{19}H_8F_{12}O_2$: C,45.99; H, 1.62; N, 0. Found: C,45.98; H, 1.62; N, 0.

3,5-(3,5-$(CF_3)_2$Ph)$_2$PzH: To the solution of 1,3-bis(3,5-bis(trifluoromethyl)phenyl)-3-hydroxyprop-2-en-1-one (4 g, 8.06 mmol) in 6 mL THF in a 50mL RBF was added hydrazine monohydrochloride (0.61 g, 8.86 mmol)) dissolved in 2.5mL DI water dropwise. After 30 minutes, product precipitates out. 5mL of THF along with 2mL of isopropanol was added to facilitate stirring. The reaction mixture was refluxed for 16 h for completion of the reaction. After the reaction is complete, ice cold DI water was added to the cold reaction mixture along with stirring. Product precipitated out and was filtered under suction in cold condition. The product was press dried and then dried under vaccuo for 30 minutes to give white product (3.5 g, 87 %). The product was recrystallized from hot chloroform as colorless shiny cubic crystals. mp 188ºC; ^{1}H NMR ($CDCl_3$, 300 MHz) 8.19 (4 H, s, ar CH), 7.90 (2 H, s, ar CH), 7.11 (1 H, s, Pz ring CH). ^{19}F NMR -62.52ppm. Anal. Calcd for $C_{19}H_8F_{12}N_2$: C,46.36; H, 1.64; N, 5.69. Found: C,46.21; H, 1.36; N, 5.80.

{[3,5-(3,5-$(CF_3)_2$Ph)$_2$Pz]Cu}$_3$: NaH (22.15 mg, 0.55 mmol, 60% in oil) was washed free from oil with dry hexane (5 mL) at 0ºC under N_2 atmosphere. Dry THF (10 mL) was added to it, followed by pyrazole (250 mg, 0.503 mmol) in dry THF (5 mL) at low temperature and let the reaction mixture stir for 30 minutes, H_2 gas evolves. Add this sodium salt of pyrazolate in THF to (158.2 mg, 0.503 mmol) of $Cu(CH_3CN)_4BF_4$ in dry THF (5 mL) at 0ºC under N_2. The reaction mixture firstly turned clear, then light green and then it turned cloudy, followed by reaction mixture turning clear with some white solid precipitating out. The reaction mixture was refluxed for 4 days under N_2 atmosphere. The mixture was cooled and filtered via cannula. The filtrate was concentrate in vaccuo to get white solid. The compound was recrystallized from toluene. ^{1}H NMR ($CDCl_3$, 300 MHz) 8.10 (4 H, s, ar CH), 7.71 (2 H, s, ar CH), 7.02 (1 H, s, Pz ring CH). ^{19}F NMR -63.05 ppm.

{[3,5-(3,5-$(CF_3)_2$Ph)$_2$Pz]Ag}$_3$: To a mixture of Ag_2O (0.13 g, 0.56 mmol) and 3,5-bis(3,5-bis(trifluoromethyl) phenyl)-1H-pyrazole (0.5 g, 1.02 mmol) was added degassed benzene (8 mL) and reaction mixture was protected from light and refluxed under N_2 atmosphere overnight. The reaction mixture was cooled to room temperature and then filtered (Celite®) under N_2 atmosphere. The black solid was discarded. The solvent was evaporated under vaccuo to give white solid. The product was recrystallized from dichloromethane: hexane 4:1 at -20^{0}C to give colorless shiny needle like crystals. ^{1}H NMR ($CDCl_3$, 300 MHz); 8.03 (4 H, s, ar CH), 7.70 (2 H, s, ar CH), 7.04 (1 H, s, Pz ring CH). ^{19}F NMR -62.88 ppm. Anal. Calcd for $C_{64}H_{29}Ag_3F_{36}N_6$: C, 40.68; N, 4.45, Found: C,40.4; N, 3.6.

{[3,5-(3,5-$(CF_3)_2$Ph)$_2$Pz]Au}$_3$: NaH (22.15 mg, 0.55 mmol, 60% in oil) was washed free from oil with dry hexane (5 mL) at 0ºC under N_2 atmosphere. Dry THF (5 mL) was added to it, followed by pyrazole (250 mg, 0.503 mmol) in dry THF (10 mL) at low temperature and let the reaction mixture stir for 30 minutes, H_2 gas evolved. Added this sodium salt of pyrazolate in THF to

Au(THT)Cl (161.25 mg, 0.503 mmol) in dry THF (10 mL) at 0ºC under N_2. The reaction mixture firstly turned light yellow and then it turned cloudy, followed by reaction mixture turning clear with some white solid precipitating out. The reaction mixture was allowed stir for 36h at room temperature. The reaction mixture was protected from light using aluminum foil. The mixture was concentrated to 5mL and 1mL hexane was added. Small amount of a white solid precipitated as the byproduct and reaction mass was filtered via cannula. The filtrate was concentrated in vaccuo to get a white solid. The compound was recrystallized from toluene. ^{1}H NMR ($CDCl_3$, 300 MHz); 8.15 (4 H, s, ar CH), 7.72 (2 H, s, ar CH), 7.17 (1 H, s, Pz ring CH). ^{19}F NMR -62.88 ppm.

CHAPTER 3

X-RAY STRUCTURE DETERMINATION OF COMPLEXES

General Procedures. Single Crystal covered with a layer of hydrocarbon oil was selected and attached to a glass fiber and immediately placed in the low temperature nitrogen stream.

X-ray studies. Single-crystal X-ray analysis of 3,5-(3,5-$(CF_3)_2Ph)_2PzH$ revealed that it crystalized in R-3 space group (**Figure 10**) and it exists as H-bonded trinuclear complex (**Figure 11**). High quality structures have been obtained for pyrazole and gold pyrazolate complex as compared to copper and silver metal pyrazolate complexes. $\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]Cu\}_3$ was obtained as a toluene solvate and reveals a trinuclear structure (**Figure 12**) and it crystalized in P-1 space group. The pyrazolyl-bridged copper ions feature a linear geometry. The nine-membered Cu_3N_6 metallacycle shows distortions. The intra trimer Cu---Cu separations within the copper triangles ("$[Cu_3]$" units) range from 3.13 to 3.44 Å. These distances are much longer than the sum of the van der Waals radii of two copper atoms (2.80 Å) or the Cu---Cu distance in the open-shell metallic copper (2.56 Å). $\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]Ag\}_3$ crystallizes in the *P-1* space group and also exist as a trimer (**Figure 13**). The intra trimer Ag---Ag separations within the silver triangles ("$[Ag_3]$" units) range from 3.36 to 3.43 Å. The N-Ag-N bond angle vary from 174.2(2) – 176.8(8)^0. $\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]Au\}_3$ also adopts a trinuclear structure (**Figure 14**) with a distorted plane of Au_3N_6 metallacycle and it crystalized in $P2_1/c$ space group. The intra trimer Au---Au separations within the gold triangles ("$[Au_3]$" units) range from 3.28 to 3.36 Å. These metal pyrazolate complexes need to be investigated for π-π stacking interactions.

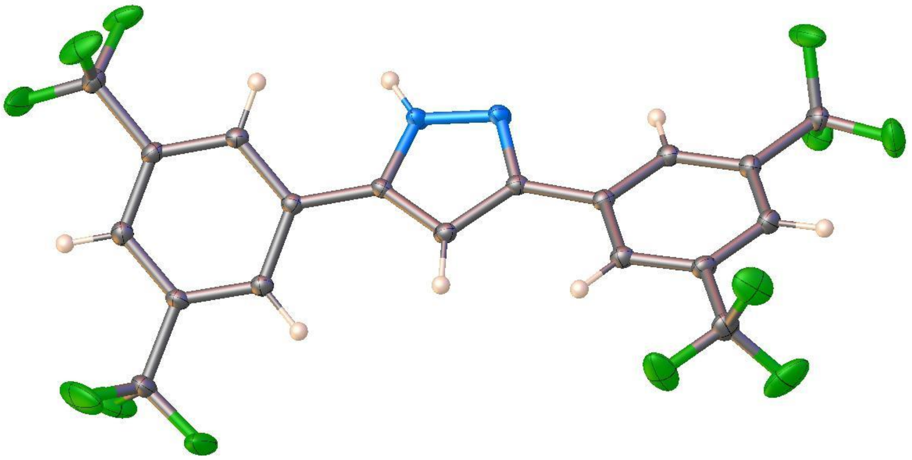


Figure 10. X-ray Structure of 3,5-(3,5-$(CF_3)_2$Ph$)_2$PzH.

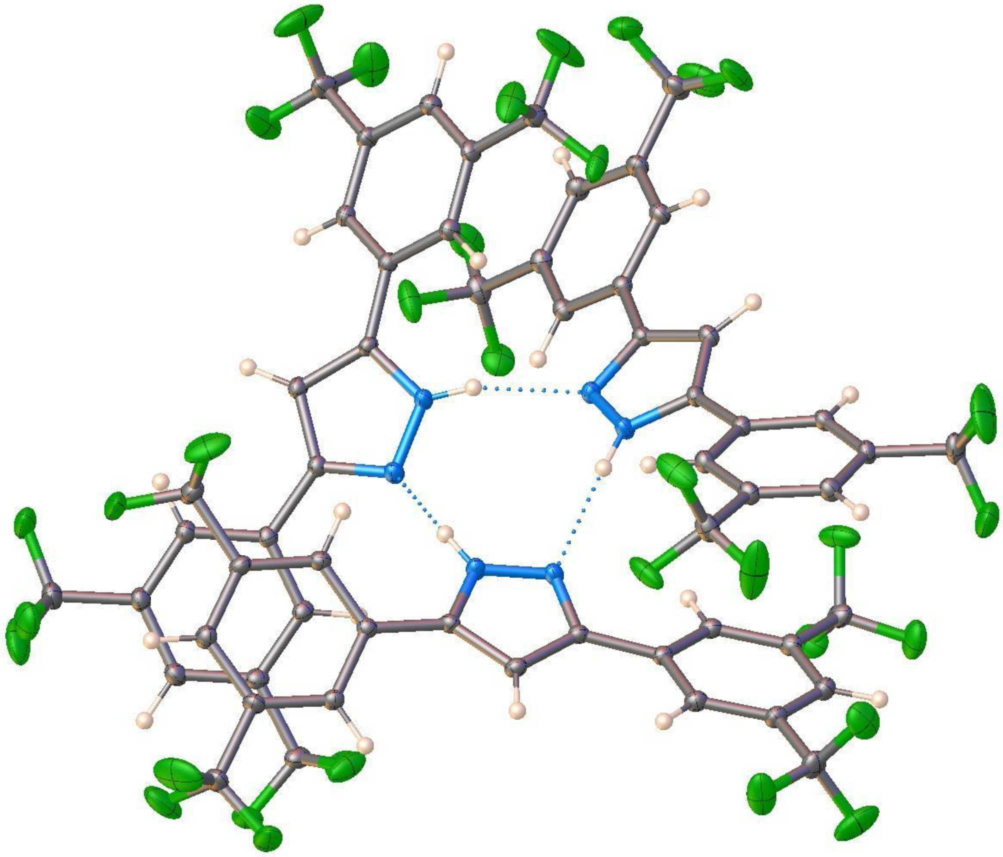


Figure 11. X-ray Structure of {[3,5-(3,5-$(CF_3)_2$Ph)$_2$Pz]H}$_3$.

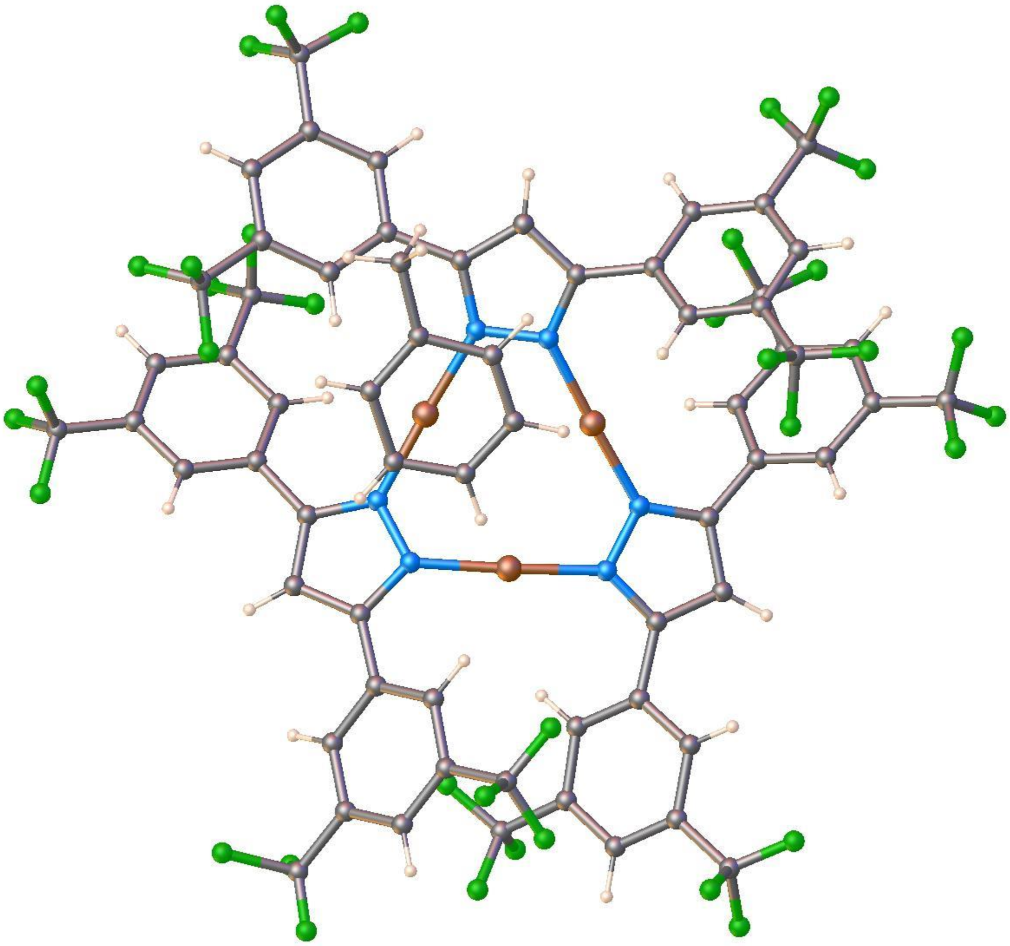


Figure 12. X-ray Structure of $\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]Cu\}_3$.

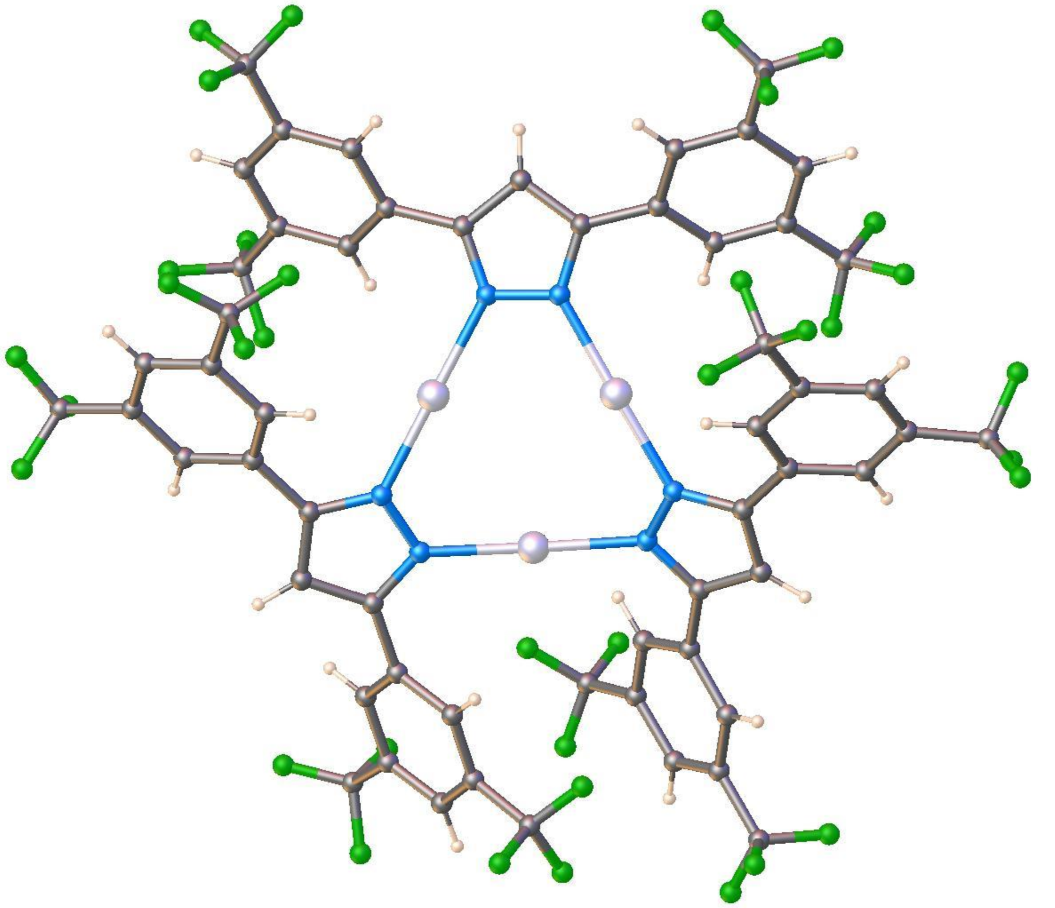


Figure 13. X-ray Structure of $\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]Ag\}_3$.

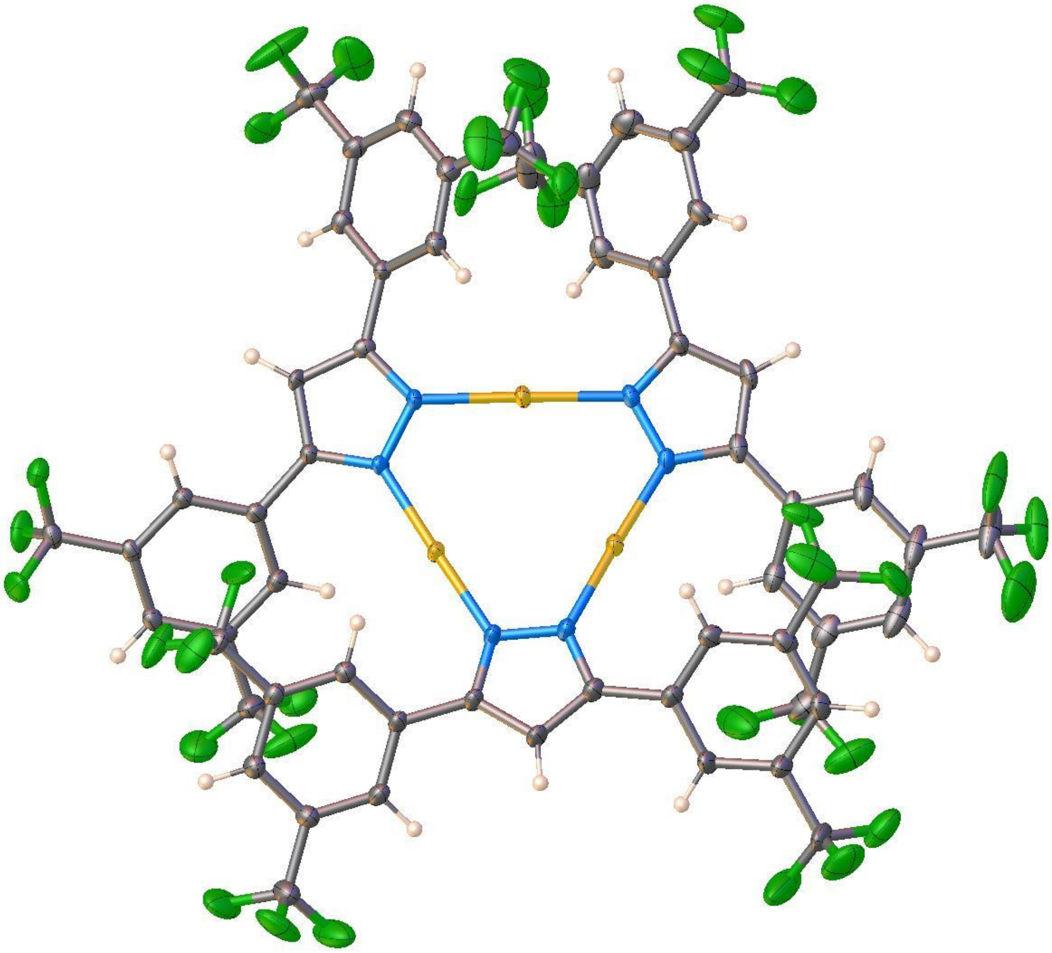


Figure 14. X-ray Structure of {[3,5-(3,5-$(CF_3)_2$Ph)$_2$Pz]Au}$_3$.

CHAPTER 4

CONCLUSION

Metal pyrazolate complexes of d-10 metal atoms are of significant interest. Although large amount of work has been done on coinage metal based pyrazolate complexes, the effects of steric environment on the pyrazolate ring have not been explored in detail using large aryl substituents. In this study, an attempt has been made to increase the steric bulk on the pyrazole ring using large fluorinated aryl groups. The 3,5-(3,5-$(CF_3)_2Ph)_2PzH$ and trinuclear copper(I), silver(I) and gold(I) complexes of 3,5-(3,5-$(CF_3)_2Ph)_2PzH$ have been synthesized and characterized by ^1H and ^{19}F NMR and X-ray crystallography studies. {[3,5-(3,5-$(CF_3)_2Ph)_2Pz]Au\}_3$ and {[3,5-(3,5-$(CF_3)_2Ph)_2Pz]Ag\}_3$ complexes were found to be light sensitive. From X-ray crystallography studies, it was found that 3,5-(3,5-$(CF_3)_2Ph)_2PzH$ existed as H-bonded trimer. Metal pyrazolate complexes of 3,5-(3,5-$(CF_3)_2Ph)_2PzH$ also existed as trimers (**Figure 12-14**) and their identity was confirmed but the trinuclear framework is distorted as compared to other previously reported metal pyrazolate complexes.[31-33] This distorted framework is attributed to the bulky substituents attached at the 3- and 5- position of the ring. These metal pyrazolate complexes didn't show the usual metal-metal interactions as the internuclear distance between the two trimeric units is very large. The metal pyrazolate complexes showed luminescence when irradiated by longer wavelength (365 nm) ultraviolet light. {[3,5-(3,5-$(CF_3)_2Ph)_2Pz]Au\}_3$ complex showed very bright blue light fluorescence at room temperature whereas {[3,5-(3,5-$(CF_3)_2Ph)_2Pz]Cu\}_3$ and {[3,5-(3,5-$(CF_3)_2Ph)_2Pz]Ag\}_3$ complexes showed light green colored fluorescence only under low temperature of 77 K when irradiated at 365 nm of UV light. The photoluminescence studies of {[3,5-(3,5-$(CF_3)_2Ph)_2Pz]Au\}_3$ (**Figure 9**) revealed that {[3,5-(3,5-$(CF_3)_2Ph)_2Pz]Au\}_3$ exhibited bright blue luminescence with emission maxima near 480-490 nm and stoke shift on the order of 2111 cm^{-1} (λ_{Exc} **=** 365 nm at RT). This stoke shift when compared to stoke shifts reported previously (>18000 $cm^{-}1$) for {[3,5-$(CF_3)_2Pz]M\}_3$ where M = Cu, Ag, Au. is much smaller. So, the excited state for $\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]Au\}_3$ is not as largely distorted as for $\{[3,5\text{-}(CF_3)_2Pz]Au\}_3$ analogues.[22] Photoluminescence properties of Cu and Ag trimers have not been studied yet and it needs to be explored to draw a comparison between the photoluminescence data of these three complexes.

APPENDIX

A. X-RAY DATA COLLECTION AND SELECTED BOND DISTANCES AND ANGLES

Table 2: Crystal data and structure refinement for [3,5-(3,5-(CF_3)$_2$Ph)$_2$Pz]H

Identification code	rad534_0m_a (1)
Empirical formula	$C_{19}H_8F_{12}N_2$
Formula weight	492.27
Temperature/K	99.99
Crystal system	trigonal
Space group	R-3
a/Å	17.7048(6)
b/Å	17.7048(6)
c/Å	31.8231(11)
α/°	90
β/°	90
γ/°	120
Volume/Å^3	8638.8(7)
Z	18
ρ_{calc}g/cm^3	1.703
μ/mm^{-1}	0.184
F(000)	4392.0
Crystal size/mm^3	0.5 × 0.41 × 0.25
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.466 to 59.264
Index ranges	-24 ≤ h ≤ 24, -24 ≤ k ≤ 24, -44 ≤ l ≤ 44
Reflections collected	36951
Independent reflections	5428 [R_{int} = 0.0228, R_{sigma} = 0.0144]
Data/restraints/parameters	5428/0/300
Goodness-of-fit on F^2	1.041
Final R indexes [I>=2σ (I)]	R_1 = 0.0332, wR_2 = 0.0889
Final R indexes [all data]	R_1 = 0.0342, wR_2 = 0.0900
Largest diff. peak/hole / e Å^{-3}	0.35/-0.41

Table 3: Bond Lengths for $[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]H$

Atom	Atom	Length/Å
F1	C10	1.3346(17)
F2	C10	1.3187(17)
F3	C10	1.3388(16)
F4	C11	1.3247(17)
F5	C11	1.3371(18)
F6	C11	1.3237(19)
F7	C18	1.3388(16)
F8	C18	1.3420(17)
F9	C18	1.3321(16)
F10	C19	1.3301(18)
F11	C19	1.3356(18)
F12	C19	1.3238(18)
N1	N2	1.3478(14)
N1	C1	1.3563(15)
N2	C3	1.3434(15)
C1	C2	1.3905(16)
C1	C4	1.4656(16)
C2	C3	1.4071(16)
C3	C12	1.4691(16)
C4	C5	1.3944(16)
C4	C9	1.4013(16)
C5	C6	1.3907(17)
C6	C7	1.3871(17)
C6	C10	1.5001(17)
C7	C8	1.3939(17)
C8	C9	1.3834(17)
C8	C11	1.5007(18)
C12	C13	1.3977(16)
C12	C17	1.4001(16)
C13	C14	1.3888(17)
C14	C15	1.3885(18)
C14	C18	1.5039(18)
C15	C16	1.3953(18)
C16	C17	1.3862(17)
C16	C19	1.5074(18)

Table 4: Bond Angles for $[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]H$.

Atom	Atom	Atom	Angle/˚
N2	N1	C1	112.37(10)
C3	N2	N1	105.30(10)
N1	C1	C2	106.48(10)
N1	C1	C4	121.14(11)
C2	C1	C4	132.38(11)
C1	C2	C3	104.97(9)
N2	C3	C2	110.88(10)
N2	C3	C12	118.78(10)
C2	C3	C12	130.34(11)
C5	C4	C1	120.33(11)
C5	C4	C9	119.19(11)
C9	C4	C1	120.46(10)
C6	C5	C4	120.14(11)
C5	C6	C10	119.20(11)
C7	C6	C5	120.99(11)
C7	C6	C10	119.74(11)
C6	C7	C8	118.48(11)
C7	C8	C11	117.90(11)
C9	C8	C7	121.40(11)
C9	C8	C11	120.68(11)
C8	C9	C4	119.75(11)
F1	C10	F3	105.30(11)
F1	C10	C6	111.26(12)
F2	C10	F1	106.72(13)
F2	C10	F3	107.88(14)
F2	C10	C6	112.96(12)
F3	C10	C6	112.27(11)
F4	C11	F5	107.36(14)
F4	C11	C8	112.97(11)
F5	C11	C8	111.59(12)
F6	C11	F4	106.99(13)
F6	C11	F5	105.72(13)
F6	C11	C8	111.80(12)
C13	C12	C3	119.70(11)
C13	C12	C17	118.99(11)
C17	C12	C3	121.31(11)
C14	C13	C12	120.17(11)
C13	C14	C18	118.24(11)
C15	C14	C13	121.22(11)
C15	C14	C18	120.52(11)
C14	C15	C16	118.29(11)
C15	C16	C19	117.74(11)
C17	C16	C15	121.34(11)
C17	C16	C19	120.91(12)
C16	C17	C12	119.95(11)
F7	C18	F8	105.64(12)
F7	C18	C14	111.95(10)
F8	C18	C14	111.27(12)
F9	C18	F7	108.07(12)
F9	C18	F8	106.46(11)
F9	C18	C14	113.01(11)
F10	C19	F11	106.25(13)
F10	C19	C16	111.43(12)
F11	C19	C16	111.19(12)
F12	C19	F10	108.45(13)
F12	C19	F11	106.50(13)
F12	C19	C16	112.69(12)

Table 5. Crystal data and structure refinement for $\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]Cu\}_3$

Identification code	rad539_0m_a (1)
Empirical formula	$C_{67.5}H_{33}Cu_3F_{36}N_6$
Formula weight	1802.62
Temperature/K	100.01
Crystal system	triclinic
Space group	P-1
a/Å	8.4054(10)
b/Å	19.555(2)
c/Å	21.674(2)
α/°	107.382(2)
β/°	91.600(2)
γ/°	98.226(2)
Volume/Å^3	3355.4(7)
Z	2
ρ_{calc}g/cm^3	1.784
μ/mm^{-1}	1.091
F(000)	1782.0
Crystal size/mm^3	0.3 × 0.07 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.654 to 52
Index ranges	$-10 \le h \le 10$, $-24 \le k \le 24$, $-26 \le l \le 26$
Reflections collected	30015
Independent reflections	13114 [R_{int} = 0.0440, R_{sigma} = 0.0620]
Data/restraints/parameters	13114/327/1104
Goodness-of-fit on F^2	1.087
Final R indexes [I>=2σ (I)]	R_1 = 0.0864, wR_2 = 0.2395
Final R indexes [all data]	R_1 = 0.1105, wR_2 = 0.2592
Largest diff. peak/hole / e Å^{-3}	2.40/-0.97

Table 6: Bond Lengths for $\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]Cu\}_3$.

Atom	Atom	Length/Å
Cu1	N1	1.869(7)
Cu1	N6	1.867(7)
Cu2	N2	1.848(7)
Cu2	N3	1.843(7)
Cu3	N4	1.849(7)
Cu3	N5	1.854(7)
F1	C10	1.333(12)
F2	C10	1.331(11)
F3	C10	1.343(12)
F4	C11	1.336(11)
F5	C11	1.330(11)
F6	C11	1.340(11)
F7	C18	1.337(12)
F8	C18	1.323(14)
F9	C18	1.339(13)
F10	C19	1.354(11)
F11	C19	1.412(12)
F12	C19	1.334(12)
F13	C29	1.325(13)
F14	C29	1.323(12)
F15	C29	1.327(13)
F16	C30	1.297(16)
F17	C30	1.312(15)
F18	C30	1.330(13)
F19	C37	1.304(12)
F20	C37	1.308(12)
F21	C37	1.318(11)
F22	C38	1.340(11)
F23	C38	1.339(11)
F24	C38	1.331(10)
F25	C48	1.305(12)
F26	C48	1.343(12)
F27	C48	1.323(14)
F28	C49	1.39(3)
F29	C49	1.21(2)
F30	C49	1.49(3)
F31	C56	1.308(12)
F32	C56	1.323(12)
F33	C56	1.332(13)
F34	C57	1.321(11)
F35	C57	1.297(12)
F36	C57	1.310(12)
N1	N2	1.363(9)
N1	C1	1.346(10)
N2	C3	1.347(10)
C14	C15	1.379(14)
C14	C18	1.504(13)
C15	C16	1.394(13)
C16	C17	1.399(12)
C16	C19	1.427(10)
C19	F11A	1.382(12)
C19	F12A	1.387(11)
C19	F10A	1.315(12)
C20	C21	1.411(11)
C20	C23	1.462(11)
C21	C22	1.385(11)
C22	C31	1.478(11)
C23	C24	1.403(12)
C23	C28	1.387(12)
C24	C25	1.391(12)
C25	C26	1.390(14)
C25	C29	1.500(13)
C26	C27	1.383(13)
C27	C28	1.392(12)
C27	C30	1.500(13)
C31	C32	1.399(11)
C31	C36	1.396(12)
C32	C33	1.406(11)
C33	C34	1.370(12)
C33	C37	1.495(12)
C34	C35	1.386(12)
C35	C36	1.390(11)
C35	C38	1.505(12)
C39	C40	1.393(11)
C39	C42	1.456(11)
C40	C41	1.377(11)
C41	C50	1.482(11)
C42	C43	1.389(12)
C42	C47	1.402(11)
C43	C44	1.402(11)
C44	C45	1.378(12)
C44	C48	1.491(13)
C45	C46	1.391(13)
C46	C47	1.393(12)
C46	C49	1.490(12)
C49	F29A	1.440(19)
C49	F28A	1.26(3)
C49	F30A	1.235(17)
C50	C51	1.398(11)
C50	C55	1.396(11)

N3	N4	1.368(9)
N3	C20	1.335(10)
N4	C22	1.346(10)
N5	N6	1.373(9)
N5	C39	1.356(10)
N6	C41	1.352(10)
C1	C2	1.390(11)
C1	C4	1.478(10)
C2	C3	1.375(11)
C3	C12	1.483(11)
C4	C5	1.385(11)
C4	C9	1.394(11)
C5	C6	1.396(12)
C6	C7	1.396(12)
C6	C10	1.488(13)
C7	C8	1.374(12)
C8	C9	1.395(11)
C8	C11	1.496(12)
C12	C13	1.386(12)
C12	C17	1.390(12)
C13	C14	1.382(12)
C51	C52	1.381(12)
C52	C53	1.403(13)
C52	C56	1.492(13)
C53	C54	1.376(13)
C54	C55	1.396(11)
C54	C57	1.489(12)
C58	C59	1.429(16)
C58	C63	1.379(16)
C58	C64	1.463(15)
C59	C60	1.344(17)
C60	C61	1.363(19)
C61	C62	1.352(19)
C62	C63	1.453(18)
C1A	C1B	1.504(19)
C1B	C1C	1.394(15)
C1B	C1G	1.391(14)
C1C	C1D	1.389(15)
C1D	C1E	1.389(15)
C1E	C1F	1.391(15)
C1F	C1G	1.386(15)

Table 7: Bond Angles for {[3,5-(3,5-$(CF_3)_2$Ph$)_2$Pz]Cu$\}_3$.

Atom	Atom	Atom	Angle/˚
N6	Cu1	N1	176.7(3)
N3	Cu2	N2	178.1(3)
N4	Cu3	N5	175.2(3)
N2	N1	Cu1	115.2(5)
C1	N1	Cu1	136.7(5)
C1	N1	N2	108.0(6)
N1	N2	Cu2	120.9(5)
C3	N2	Cu2	129.8(5)
C3	N2	N1	108.5(6)
N4	N3	Cu2	119.4(5)
C20	N3	Cu2	130.2(5)
C20	N3	N4	108.9(6)
N3	N4	Cu3	116.6(5)
C22	N4	Cu3	135.8(6)
C22	N4	N3	107.4(6)
N6	N5	Cu3	118.4(5)
C39	N5	Cu3	130.8(6)
C39	N5	N6	108.6(6)
N5	N6	Cu1	118.4(5)
C41	N6	Cu1	131.3(6)
C41	N6	N5	107.2(6)
N1	C1	C2	108.8(7)
N1	C1	C4	122.9(7)
C2	C1	C4	128.2(7)
C3	C2	C1	105.8(7)
N2	C3	C2	109.0(7)
N2	C3	C12	121.4(7)
C2	C3	C12	129.6(7)
C5	C4	C1	121.9(7)
C5	C4	C9	119.8(7)
C9	C4	C1	118.2(7)
C4	C5	C6	119.7(8)
C5	C6	C7	120.7(8)
C5	C6	C10	119.8(8)
C7	C6	C10	119.3(8)
C8	C7	C6	118.9(7)
C7	C8	C9	121.1(7)
C7	C8	C11	119.0(7)
C9	C8	C11	119.9(8)
C4	C9	C8	119.8(7)
F1	C10	F3	106.8(8)
F1	C10	C6	111.8(7)
F2	C10	F1	105.9(8)
F2	C10	F3	105.9(7)
F2	C10	C6	113.4(7)
F16	C30	F17	107.6(11)
F16	C30	F18	105.1(9)
F16	C30	C27	112.0(11)
F17	C30	F18	107.2(12)
F17	C30	C27	112.1(9)
F18	C30	C27	112.5(8)
C32	C31	C22	118.4(7)
C36	C31	C22	121.6(7)
C36	C31	C32	119.8(7)
C31	C32	C33	119.1(8)
C32	C33	C37	119.1(8)
C34	C33	C32	121.3(8)
C34	C33	C37	119.5(8)
C33	C34	C35	118.8(8)
C34	C35	C36	121.7(8)
C34	C35	C38	118.6(8)
C36	C35	C38	119.7(8)
C35	C36	C31	119.2(8)
F19	C37	F20	108.4(10)
F19	C37	F21	105.9(8)
F19	C37	C33	113.3(8)
F20	C37	F21	103.1(9)
F20	C37	C33	113.7(8)
F21	C37	C33	111.7(8)
F22	C38	C35	112.2(7)
F23	C38	F22	106.3(7)
F23	C38	C35	111.3(8)
F24	C38	F22	107.4(8)
F24	C38	F23	107.3(7)
F24	C38	C35	112.1(7)
N5	C39	C40	108.5(7)
N5	C39	C42	123.0(7)
C40	C39	C42	128.5(7)
C41	C40	C39	105.7(7)
N6	C41	C40	110.0(7)
N6	C41	C50	121.4(7)
C40	C41	C50	128.5(7)
C43	C42	C39	121.6(7)
C43	C42	C47	118.7(7)
C47	C42	C39	119.7(7)
C42	C43	C44	120.1(8)
C43	C44	C48	119.8(8)
C45	C44	C43	121.6(8)
C45	C44	C48	118.6(8)
C44	C45	C46	118.2(8)

F3	C10	C6	112.5(9)	C45	C46	C47	121.3(8)
F4	C11	F6	105.4(7)	C45	C46	C49	119.5(8)
F4	C11	C8	112.6(8)	C47	C46	C49	119.2(8)
F5	C11	F4	105.8(8)	C46	C47	C42	120.1(8)
F5	C11	F6	106.8(8)	F25	C48	F26	106.8(10)
F5	C11	C8	114.2(7)	F25	C48	F27	108.5(10)
F6	C11	C8	111.3(8)	F25	C48	C44	112.5(8)
C13	C12	C3	119.8(8)	F26	C48	C44	111.3(9)
C13	C12	C17	119.4(8)	F27	C48	F26	104.6(8)
C17	C12	C3	120.8(8)	F27	C48	C44	112.6(9)
C14	C13	C12	119.7(8)	F28	C49	F30	96(3)
C13	C14	C18	120.3(9)	F28	C49	C46	105.1(19)
C15	C14	C13	121.1(9)	F29	C49	F28	117(3)
C15	C14	C18	118.6(8)	F29	C49	F30	105.1(17)
C14	C15	C16	120.1(8)	F29	C49	C46	120.9(14)
C15	C16	C17	118.5(8)	F30	C49	C46	109.8(10)
C15	C16	C19	120.9(8)	F29A	C49	C46	108.1(11)
C17	C16	C19	120.6(8)	F28A	C49	C46	117.2(19)
C12	C17	C16	121.1(8)	F28A	C49	F29A	99(3)
F7	C18	F9	106.4(10)	F30A	C49	C46	113.6(10)
F7	C18	C14	113.1(8)	F30A	C49	F29A	102.6(12)
F8	C18	F7	107.7(9)	F30A	C49	F28A	113.6(19)
F8	C18	F9	106.1(9)	C51	C50	C41	118.7(7)
F8	C18	C14	112.4(10)	C55	C50	C41	122.0(7)
F9	C18	C14	110.7(9)	C55	C50	C51	119.2(7)
F10	C19	F11	98.4(10)	C52	C51	C50	120.7(8)
F10	C19	C16	116.1(9)	C51	C52	C53	120.4(8)
F11	C19	C16	110.6(9)	C51	C52	C56	120.3(8)
F12	C19	F10	110.6(12)	C53	C52	C56	119.3(8)
F12	C19	F11	104.0(11)	C54	C53	C52	118.6(8)
F12	C19	C16	115.2(11)	C53	C54	C55	121.7(8)
F11A	C19	C16	112.7(9)	C53	C54	C57	119.0(8)
F11A	C19	F12A	98.5(10)	C55	C54	C57	119.3(8)
F12A	C19	C16	112.3(9)	C50	C55	C54	119.4(8)
F10A	C19	C16	117.7(10)	F31	C56	F32	106.2(9)
F10A	C19	F11A	106.0(11)	F31	C56	F33	108.3(10)
F10A	C19	F12A	107.8(11)	F31	C56	C52	113.2(9)
N3	C20	C21	109.2(7)	F32	C56	F33	102.7(10)
N3	C20	C23	122.2(7)	F32	C56	C52	113.7(8)
C21	C20	C23	128.5(7)	F33	C56	C52	112.1(8)
C22	C21	C20	104.1(7)	F34	C57	C54	112.8(8)
N4	C22	C21	110.4(7)	F35	C57	F34	106.5(9)
N4	C22	C31	122.6(7)	F35	C57	F36	107.2(10)
C21	C22	C31	127.0(7)	F35	C57	C54	112.8(8)
C24	C23	C20	120.6(7)	F36	C57	F34	102.9(9)
C28	C23	C20	120.7(7)	F36	C57	C54	113.8(7)
C28	C23	C24	118.7(8)	C59	C58	C64	118.6(11)
C25	C24	C23	120.0(8)	C63	C58	C59	115.6(10)

C24	C25	C29	119.0(9)	C63	C58	C64	125.8(12)
C26	C25	C24	120.7(8)	C60	C59	C58	122.8(12)
C26	C25	C29	120.3(8)	C59	C60	C61	120.2(13)
C27	C26	C25	119.4(8)	C62	C61	C60	121.9(13)
C26	C27	C28	120.2(8)	C61	C62	C63	118.0(12)
C26	C27	C30	118.8(8)	C58	C63	C62	121.3(12)
C28	C27	C30	121.0(8)	C1C	C1B	C1A	120.6(14)
C23	C28	C27	121.1(8)	C1G	C1B	C1A	120.4(15)
F13	C29	F15	104.4(9)	C1G	C1B	C1C	119.0(13)
F13	C29	C25	113.6(8)	C1D	C1C	C1B	120.4(14)
F14	C29	F13	105.8(10)	C1C	C1D	C1E	120.3(14)
F14	C29	F15	107.4(9)	C1D	C1E	C1F	119.1(14)
F14	C29	C25	112.8(9)	C1G	C1F	C1E	120.6(14)
F15	C29	C25	112.2(9)	C1F	C1G	C1B	120.5(14)

Table 8: Crystal data and structure refinement for {[3,5-(3,5-$(CF_3)_2$Ph)$_2$Pz]Ag}$_3$.

Identification code	rad378_0m_a
Empirical formula	$C_{59}H_{25}Ag_3Cl_4F_{36}N_6$
Formula weight	1967.26
Temperature/K	299.06
Crystal system	triclinic
Space group	P-1
a/Å	8.6941(5)
b/Å	15.8573(8)
c/Å	26.1433(13)
α/°	89.287(2)
β/°	85.728(2)
γ/°	87.428(2)
Volume/Å^3	3590.5(3)
Z	2
ρ_{calc}g/cm^3	1.820
μ/mm^{-1}	1.095
F(000)	1908.0
Crystal size/mm^3	0.19 × 0.15 × 0.09
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.768 to 52.998
Index ranges	$-10 \le h \le 10$, $-19 \le k \le 19$, $-32 \le l \le 32$
Reflections collected	37199
Independent reflections	14836 [R_{int} = 0.0332, R_{sigma} = 0.0407]
Data/restraints/parameters	14836/1941/1225
Goodness-of-fit on F^2	1.026
Final R indexes [I>=2σ (I)]	R_1 = 0.0671, wR_2 = 0.1912
Final R indexes [all data]	R_1 = 0.1006, wR_2 = 0.2182
Largest diff. peak/hole / e Å^{-3}	1.13/-0.85

Table 9: Bond Lengths for $\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]Ag\}_3$.

Atom	Atom	Length/Å
Ag1	N1	2.082(5)
Ag1	N6	2.073(5)
Ag2	Ag3	3.3678(7)
Ag2	N2	2.081(5)
Ag2	N3	2.084(5)
Ag3	N4	2.090(5)
Ag3	N5	2.076(5)
F4	C11	1.318(6)
F5	C11	1.306(6)
F6	C11	1.310(6)
F7	C17	1.313(6)
F8	C17	1.320(6)
F9	C17	1.298(6)
F10	C18	1.306(5)
F11	C18	1.311(6)
F12	C18	1.313(5)
F13	C28	1.308(5)
F14	C28	1.310(5)
F15	C28	1.301(5)
F16	C29	1.323(6)
F17	C29	1.306(6)
F18	C29	1.304(6)
F19	C36	1.314(6)
F20	C36	1.306(6)
F21	C36	1.314(6)
F25	C47	1.308(6)
F26	C47	1.306(6)
F27	C47	1.314(6)
F28	C48	1.316(5)
F29	C48	1.314(5)
F30	C48	1.312(5)
F31	C55	1.307(6)
F32	C55	1.315(6)
F33	C55	1.314(6)
F34	C56	1.312(5)
F35	C56	1.312(5)
F36	C56	1.308(5)
N1	N2	1.369(8)
N1	C1	1.342(7)
N2	C3	1.335(8)
N3	N4	1.353(7)
N3	C19	1.356(8)
N4	C21	1.328(8)
N5	N6	1.355(6)
N5	C38	1.350(7)
C17	F9A	1.325(6)
C19	C20	1.372(9)
C19	C22	1.466(9)
C20	C21	1.381(9)
C21	C30	1.480(8)
C22	C23	1.393(10)
C22	C27	1.390(10)
C23	C24	1.375(10)
C24	C25	1.359(12)
C24	C28	1.445(11)
C25	C26	1.388(12)
C26	C27	1.380(10)
C26	C29	1.484(12)
C29	F18A	1.326(6)
C29	F17A	1.300(6)
C29	F16A	1.311(6)
C30	C31	1.397(9)
C30	C35	1.375(10)
C31	C32	1.359(9)
C32	C33	1.375(11)
C32	C36	1.519(11)
C33	C34	1.361(12)
C34	C35	1.381(10)
C34	C37	1.455(13)
C36	F20A	1.319(6)
C36	F21A	1.307(6)
C36	F19A	1.311(6)
C38	C39	1.372(8)
C38	C41	1.484(8)
C39	C40	1.388(8)
C40	C49	1.479(8)
C41	C42	1.377(9)
C41	C46	1.396(9)
C42	C43	1.388(9)
C43	C44	1.368(11)
C43	C47	1.499(11)
C44	C45	1.361(12)
C45	C46	1.372(9)
C45	C48	1.495(11)
C47	F25A	1.303(6)
C47	F27A	1.309(6)
C47	F26A	1.315(6)
C49	C50	1.379(9)
C49	C54	1.400(9)
C50	C51	1.394(10)

N6	C40	1.327(8)
C1	C2	1.393(9)
C1	C4	1.457(9)
C01F	C12	1.374(10)
C01F	C16	1.385(11)
C2	C3	1.382(9)
C3	C12	1.473(10)
C4	C5	1.399(10)
C4	C9	1.398(9)
C5	C6	1.364(11)
C6	C7	1.399(11)
C6	C10	1.503(12)
C7	C8	1.360(12)
C8	C9	1.396(10)
C8	C11	1.478(10)
C11	F6A	1.317(6)
C11	F5A	1.313(6)
C11	F4A	1.307(6)
C12	C13	1.405(9)
C13	C14	1.401(12)
C14	C15	1.364(13)
C14	C17	1.501(13)
C15	C16	1.364(12)
C16	C18	1.473(12)
C17	F7A	1.302(6)
C17	F8A	1.306(6)
C51	C52	1.360(11)
C51	C55	1.530(12)
C52	C53	1.387(10)
C53	C54	1.374(9)
C53	C56	1.503(10)
C55	F31A	1.312(6)
C55	F32A	1.319(6)
C55	F33A	1.309(6)
Cl1	C57	1.761(2)
Cl2	C57	1.759(2)
Cl3	C58	1.760(2)
Cl4	C58	1.760(2)
Cl3A	C58A	1.760(2)
C58A	Cl4A	1.760(2)
F2	C10	1.315(6)
F3	C10	1.310(6)
F1	C10	1.321(6)
C10	F2A	1.320(6)
C10	F1A	1.308(6)
C10	F3A	1.310(6)
F24	C37	1.356(6)
F23	C37	1.358(6)
C37	F22	1.346(6)
C37	F24A	1.333(7)
C37	F23A	1.356(7)
C37	F22A	1.381(7)

Table 10: Bond Angles for {[3,5-(3,5-$(CF_3)_2$Ph$)_2$Pz]Ag$\}_3$.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
N6	Ag1	N1	174.8(2)	F16A	C29	C26	116.1(10)
N2	Ag2	Ag3	118.77(15)	F16A	C29	F18A	104.8(13)
N2	Ag2	N3	174.2(2)	C31	C30	C21	120.3(6)
N3	Ag2	Ag3	61.10(15)	C35	C30	C21	121.7(6)
N4	Ag3	Ag2	61.12(14)	C35	C30	C31	117.9(6)
N5	Ag3	Ag2	118.75(13)	C32	C31	C30	119.8(7)
N5	Ag3	N4	176.9(2)	C31	C32	C33	122.1(7)
N2	N1	Ag1	116.8(4)	C31	C32	C36	119.2(7)
C1	N1	Ag1	130.8(5)	C33	C32	C36	118.7(6)
C1	N1	N2	108.3(5)	C34	C33	C32	118.4(7)
N1	N2	Ag2	116.3(4)	C33	C34	C35	120.5(7)
C3	N2	Ag2	132.2(5)	C33	C34	C37	121.1(7)
C3	N2	N1	108.6(5)	C35	C34	C37	118.3(8)
N4	N3	Ag2	119.0(4)	C30	C35	C34	121.3(7)
N4	N3	C19	108.3(5)	F19	C36	C32	113.6(7)
C19	N3	Ag2	132.7(4)	F20	C36	F19	106.8(10)
N3	N4	Ag3	118.5(4)	F20	C36	F21	108.1(11)
C21	N4	Ag3	132.8(4)	F20	C36	C32	113.1(9)
C21	N4	N3	108.5(5)	F21	C36	F19	100.1(10)
N6	N5	Ag3	119.3(4)	F21	C36	C32	114.1(7)
C38	N5	Ag3	130.8(4)	F20A	C36	C32	108.2(10)
C38	N5	N6	107.9(5)	F21A	C36	C32	116.9(13)
N5	N6	Ag1	119.4(4)	F21A	C36	F20A	103.7(17)
C40	N6	Ag1	132.5(4)	F21A	C36	F19A	118.8(16)
C40	N6	N5	108.1(5)	F19A	C36	C32	107.9(10)
N1	C1	C2	108.2(6)	F19A	C36	F20A	99.1(13)
N1	C1	C4	122.7(6)	N5	C38	C39	109.6(5)
C2	C1	C4	129.0(5)	N5	C38	C41	120.8(5)
C12	C01F	C16	121.3(7)	C39	C38	C41	129.6(5)
C3	C2	C1	106.0(5)	C38	C39	C40	104.4(5)
N2	C3	C2	108.8(6)	N6	C40	C39	110.1(5)
N2	C3	C12	122.6(6)	N6	C40	C49	122.1(5)
C2	C3	C12	128.5(6)	C39	C40	C49	127.8(6)
C5	C4	C1	121.4(6)	C42	C41	C38	121.3(6)
C9	C4	C1	120.4(6)	C42	C41	C46	118.5(6)
C9	C4	C5	118.2(7)	C46	C41	C38	120.2(6)
C6	C5	C4	121.3(7)	C41	C42	C43	120.6(7)
C5	C6	C7	119.8(7)	C42	C43	C47	118.5(7)
C5	C6	C10	118.9(7)	C44	C43	C42	120.0(7)
C7	C6	C10	121.2(7)	C44	C43	C47	121.5(7)
C8	C7	C6	120.2(7)	C45	C44	C43	119.8(7)
C7	C8	C9	120.3(7)	C44	C45	C46	121.1(7)
C7	C8	C11	120.6(7)	C44	C45	C48	121.5(6)
C9	C8	C11	119.1(7)	C46	C45	C48	117.4(7)
C8	C9	C4	120.2(7)	C45	C46	C41	120.0(7)

F4	C11	C8	110.7(8)	F25	C47	F27	122.4(13)
F5	C11	F4	109.1(10)	F25	C47	C43	109.8(10)
F5	C11	F6	106.7(10)	F26	C47	F25	96.2(13)
F5	C11	C8	112.8(8)	F26	C47	F27	103.7(12)
F6	C11	F4	104.7(10)	F26	C47	C43	111.9(9)
F6	C11	C8	112.4(7)	F27	C47	C43	111.4(8)
F6A	C11	C8	113.3(9)	F25A	C47	C43	115.3(8)
F5A	C11	C8	109.9(10)	F25A	C47	F27A	111.8(11)
F5A	C11	F6A	97.3(13)	F25A	C47	F26A	108.2(10)
F4A	C11	C8	119.5(10)	F27A	C47	C43	116.7(8)
F4A	C11	F6A	103.7(14)	F27A	C47	F26A	93.8(11)
F4A	C11	F5A	110.8(14)	F26A	C47	C43	108.5(9)
C01F	C12	C3	122.0(6)	F28	C48	C45	113.8(6)
C01F	C12	C13	118.6(7)	F29	C48	F28	102.5(7)
C13	C12	C3	119.5(7)	F29	C48	C45	112.7(6)
C14	C13	C12	119.0(8)	F30	C48	F28	103.9(8)
C13	C14	C17	116.4(9)	F30	C48	F29	110.2(7)
C15	C14	C13	121.0(7)	F30	C48	C45	112.9(7)
C15	C14	C17	122.6(8)	C50	C49	C40	119.7(6)
C14	C15	C16	119.9(8)	C50	C49	C54	118.8(6)
C01F	C16	C18	120.1(7)	C54	C49	C40	121.4(6)
C15	C16	C01F	120.2(8)	C49	C50	C51	120.4(7)
C15	C16	C18	119.7(8)	C50	C51	C55	116.8(7)
F7	C17	F8	100.3(13)	C52	C51	C50	120.7(7)
F7	C17	C14	115.3(10)	C52	C51	C55	122.3(7)
F8	C17	C14	108.5(11)	C51	C52	C53	119.2(6)
F9	C17	F7	108.8(12)	C52	C53	C56	121.0(6)
F9	C17	F8	107.0(13)	C54	C53	C52	121.1(6)
F9	C17	C14	115.6(9)	C54	C53	C56	117.9(6)
F7A	C17	C14	112.5(10)	C53	C54	C49	119.8(6)
F7A	C17	F8A	115.0(13)	F31	C55	F32	106.9(12)
F7A	C17	F9A	110.2(13)	F31	C55	F33	109.6(14)
F8A	C17	C14	111.2(10)	F31	C55	C51	114.9(9)
F8A	C17	F9A	97.7(12)	F32	C55	C51	109.2(9)
F9A	C17	C14	109.1(10)	F33	C55	F32	108.0(13)
F10	C18	F11	104.5(9)	F33	C55	C51	108.1(10)
F10	C18	F12	107.6(8)	F31A	C55	C51	110.1(9)
F10	C18	C16	111.8(7)	F31A	C55	F32A	103.9(13)
F11	C18	F12	100.8(8)	F32A	C55	C51	114.5(9)
F11	C18	C16	114.7(7)	F33A	C55	C51	111.3(9)
F12	C18	C16	116.3(8)	F33A	C55	F31A	103.0(12)
N3	C19	C20	108.1(6)	F33A	C55	F32A	113.2(13)
N3	C19	C22	121.3(6)	F34	C56	F35	107.0(6)
C20	C19	C22	130.6(6)	F34	C56	C53	113.1(6)
C19	C20	C21	106.1(6)	F35	C56	C53	110.9(5)
N4	C21	C20	109.0(5)	F36	C56	F34	105.1(6)
N4	C21	C30	121.6(6)	F36	C56	F35	107.2(7)
C20	C21	C30	129.3(6)	F36	C56	C53	113.0(5)

C23	C22	C19	121.4(7)
C27	C22	C19	119.8(6)
C27	C22	C23	118.8(6)
C24	C23	C22	120.4(8)
C23	C24	C28	121.1(8)
C25	C24	C23	120.5(7)
C25	C24	C28	118.3(7)
C24	C25	C26	120.2(7)
C25	C26	C29	121.2(7)
C27	C26	C25	119.8(8)
C27	C26	C29	119.0(7)
C26	C27	C22	120.3(7)
F13	C28	F14	97.8(8)
F13	C28	C24	115.6(7)
F14	C28	C24	116.6(8)
F15	C28	F13	110.4(9)
F15	C28	F14	100.5(8)
F15	C28	C24	113.9(7)
F16	C29	C26	110.8(8)
F17	C29	F16	96.8(11)
F17	C29	C26	112.1(9)
F18	C29	F16	100.2(11)
F18	C29	F17	119.2(12)
F18	C29	C26	115.0(8)
F18A	C29	C26	108.2(9)
F17A	C29	C26	117.0(11)
F17A	C29	F18A	99.2(13)
F17A	C29	F16A	109.4(14)
Cl2	C57	Cl1	111.8(3)
Cl3	C58	Cl4	112.7(3)
Cl4A	C58A	Cl3A	112.7(3)
F2	C10	C6	110.5(8)
F2	C10	F1	106.0(11)
F3	C10	C6	112.8(9)
F3	C10	F2	105.8(12)
F3	C10	F1	111.2(12)
F1	C10	C6	110.3(9)
F2A	C10	C6	110.7(12)
F1A	C10	C6	114.0(12)
F1A	C10	F2A	103.5(15)
F1A	C10	F3A	115.9(15)
F3A	C10	C6	115.5(10)
F3A	C10	F2A	94.5(15)
F24	C37	C34	112.6(8)
F24	C37	F23	103.9(7)
F23	C37	C34	109.4(9)
F22	C37	C34	118.3(9)
F22	C37	F24	105.4(7)
F22	C37	F23	106.1(7)
F24A	C37	C34	116.4(8)
F24A	C37	F23A	107.2(7)
F24A	C37	F22A	105.1(7)
F23A	C37	C34	115.0(8)
F23A	C37	F22A	101.3(6)
F22A	C37	C34	110.3(8)

Table 11: Crystal data and structure refinement for $\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]Au\}_3$.

Identification code	Rad533_0m_a_sq (3)
Empirical formula	$C_{57}H_{21}Au_3F_{36}N_6$
Formula weight	2064.70
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	8.3667(5)
b/Å	31.7232(19)
c/Å	25.7197(15)
α/°	90
β/°	91.507(2)
γ/°	90
Volume/Å^3	6824.1(7)
Z	4
ρ_{calc}g/cm^3	2.010
μ/mm^{-1}	6.573
F(000)	3864.0
Crystal size/mm^3	0.28 × 0.15 × 0.09
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.694 to 60.054
Index ranges	$-11 \leq h \leq 11$, $-44 \leq k \leq 44$, $-36 \leq l \leq 36$
Reflections collected	89629
Independent reflections	19862 [R_{int} = 0.0345, R_{sigma} = 0.0273]
Data/restraints/parameters	19862/366/1031
Goodness-of-fit on F^2	1.069
Final R indexes [I>=2σ (I)]	R_1 = 0.0317, wR_2 = 0.0664
Final R indexes [all data]	R_1 = 0.0412, wR_2 = 0.0702
Largest diff. peak/hole / e Å^{-3}	1.84/-1.66

Table 12: Bond Lengths for $\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]Au\}_3$

Atom	Atom	Length/Å
Au1	Au2	3.3693(3)
Au1	Au3	3.2971(3)
Au1	N1	2.010(3)
Au1	N6	2.005(3)
Au2	Au3	3.2876(2)
Au2	N2	2.013(3)
Au2	N3	2.005(3)
Au3	N4	1.996(3)
Au3	N5	1.996(3)
F1	C10	1.365(6)
F2	C10	1.317(6)
F3	C10	1.307(6)
F4	C11	1.342(5)
F5	C11	1.339(5)
F6	C11	1.334(5)
F7	C18	1.319(6)
F8	C18	1.303(6)
F9	C18	1.330(6)
F10	C19	1.329(6)
F11	C19	1.349(6)
F12	C19	1.305(7)
F13	C29	1.314(11)
F14	C29	1.315(9)
F15	C29	1.468(10)
F16	C30	1.396(9)
F17	C30	1.321(9)
F18	C30	1.300(9)
F19	C37	1.279(9)
F20	C37	1.280(7)
F21	C37	1.433(9)
F22	C38	1.333(7)
F23	C38	1.328(6)
F24	C38	1.336(6)
F25	C48	1.339(6)
F26	C48	1.331(5)
F27	C48	1.335(6)
F28	C49	1.320(8)
F29	C49	1.332(7)
F30	C49	1.293(6)
F31	C56	1.304(8)
F32	C56	1.397(7)
F33	C56	1.312(7)
C7	C8	1.395(6)
C8	C9	1.392(5)
C8	C11	1.494(5)
C12	C13	1.393(5)
C12	C17	1.395(5)
C13	C14	1.385(6)
C14	C15	1.392(6)
C14	C18	1.502(6)
C15	C16	1.381(6)
C16	C17	1.395(6)
C16	C19	1.499(6)
C20	C21	1.387(5)
C20	C23	1.463(6)
C21	C22	1.388(6)
C22	C31	1.466(6)
C23	C24	1.395(6)
C23	C28	1.399(6)
C24	C25	1.391(7)
C25	C26	1.389(8)
C25	C29	1.471(6)
C26	C27	1.394(7)
C27	C28	1.391(6)
C27	C30	1.452(6)
C29	F13A	1.345(10)
C29	F15A	1.275(9)
C29	F14A	1.432(10)
C30	F16A	1.312(11)
C30	F18A	1.310(9)
C30	F17A	1.397(9)
C31	C32	1.393(5)
C31	C36	1.396(6)
C32	C33	1.398(7)
C33	C34	1.389(8)
C33	C37	1.464(6)
C34	C35	1.389(7)
C35	C36	1.392(6)
C35	C38	1.489(8)
C37	F19A	1.419(11)
C37	F21A	1.259(11)
C37	F20A	1.286(9)
C39	C40	1.387(6)
C39	C42	1.473(5)

F34	C57	1.318(5)	C40	C41	1.393(5)
F35	C57	1.329(5)	C41	C50	1.469(5)
F36	C57	1.326(5)	C42	C43	1.388(6)
N1	N2	1.363(4)	C42	C47	1.392(6)
N1	C1	1.348(4)	C43	C44	1.389(6)
N2	C3	1.340(5)	C44	C45	1.374(6)
N3	N4	1.365(5)	C44	C48	1.501(6)
N3	C20	1.346(5)	C45	C46	1.383(6)
N4	C22	1.351(5)	C46	C47	1.393(6)
N5	N6	1.364(4)	C46	C49	1.509(6)
N5	C39	1.350(5)	C50	C51	1.392(6)
N6	C41	1.351(5)	C50	C55	1.395(5)
C1	C2	1.388(5)	C51	C52	1.389(6)
C1	C4	1.474(5)	C52	C53	1.390(6)
C2	C3	1.384(5)	C52	C56	1.466(6)
C3	C12	1.477(5)	C53	C54	1.387(6)
C4	C5	1.384(5)	C54	C55	1.385(5)
C4	C9	1.397(5)	C54	C57	1.499(5)
C5	C6	1.391(6)	C56	F33A	1.270(10)
C6	C7	1.382(5)	C56	F32A	1.337(11)
C6	C10	1.509(6)	C56	F31A	1.379(11)

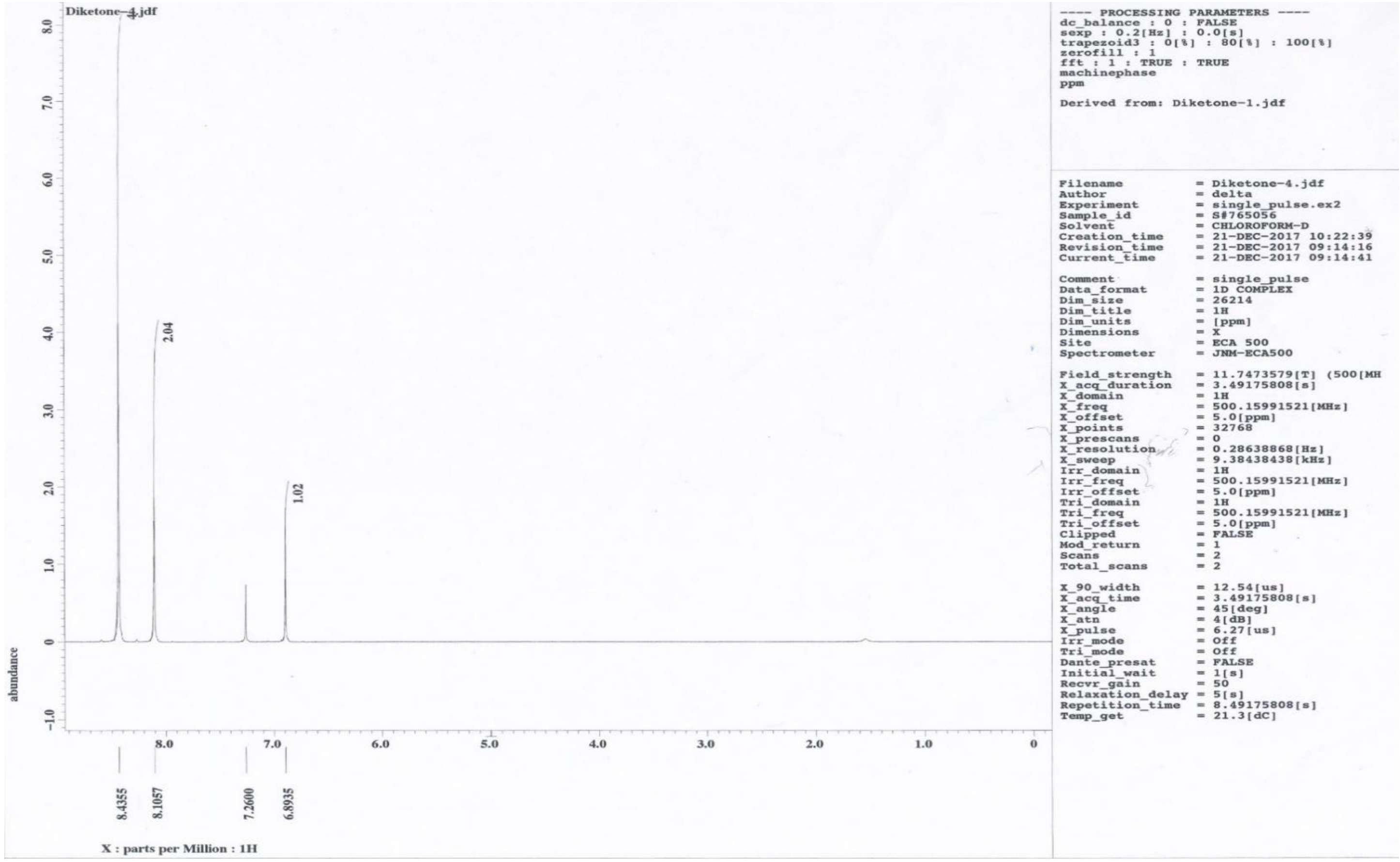
Table 13: Bond Angles for $\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]Au\}_3$

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
Au3	Au1	Au2	59.085(4)	F14	C29	F15	100.6(7)
N1	Au1	Au2	59.53(9)	F14	C29	C25	117.2(7)
N1	Au1	Au3	118.10(9)	F15	C29	C25	107.2(6)
N6	Au1	Au2	119.51(9)	F13A	C29	C25	109.5(9)
N6	Au1	Au3	61.41(9)	F13A	C29	F14A	102.2(9)
N6	Au1	N1	177.13(14)	F15A	C29	C25	116.8(7)
Au3	Au2	Au1	59.362(6)	F15A	C29	F13A	112.3(12)
N2	Au2	Au1	59.14(9)	F15A	C29	F14A	106.1(7)
N2	Au2	Au3	118.43(9)	F14A	C29	C25	108.8(7)
N3	Au2	Au1	120.10(10)	F16	C30	C27	110.6(5)
N3	Au2	Au3	61.10(10)	F17	C30	F16	100.2(8)
N3	Au2	N2	176.66(14)	F17	C30	C27	114.6(8)
Au2	Au3	Au1	61.552(5)	F18	C30	F16	104.4(8)
N4	Au3	Au1	121.50(9)	F18	C30	F17	108.8(9)
N4	Au3	Au2	61.14(9)	F18	C30	C27	116.5(6)
N4	Au3	N5	177.28(14)	F16A	C30	C27	117.3(11)
N5	Au3	Au1	60.69(9)	F16A	C30	F17A	102.6(10)
N5	Au3	Au2	120.61(9)	F18A	C30	C27	113.6(6)
N2	N1	Au1	117.7(2)	F18A	C30	F16A	112.2(11)
C1	N1	Au1	132.3(3)	F18A	C30	F17A	99.2(9)
C1	N1	N2	108.2(3)	F17A	C30	C27	109.7(7)
N1	N2	Au2	118.5(2)	C32	C31	C22	119.7(4)
C3	N2	Au2	131.3(3)	C32	C31	C36	118.9(4)
C3	N2	N1	108.1(3)	C36	C31	C22	121.4(4)
N4	N3	Au2	118.1(2)	C31	C32	C33	120.1(5)
C20	N3	Au2	133.4(3)	C32	C33	C37	119.9(5)
C20	N3	N4	108.5(3)	C34	C33	C32	120.8(4)
N3	N4	Au3	118.6(2)	C34	C33	C37	119.3(5)
C22	N4	Au3	131.1(3)	C35	C34	C33	119.0(4)
C22	N4	N3	108.3(3)	C34	C35	C36	120.5(5)
N6	N5	Au3	120.0(2)	C34	C35	C38	120.6(4)
C39	N5	Au3	131.2(3)	C36	C35	C38	118.8(4)
C39	N5	N6	108.6(3)	C35	C36	C31	120.7(4)
N5	N6	Au1	117.6(2)	F19	C37	F20	116.6(9)
C41	N6	Au1	134.0(3)	F19	C37	F21	99.8(8)
C41	N6	N5	108.4(3)	F19	C37	C33	113.0(6)
N1	C1	C2	109.0(3)	F20	C37	F21	99.5(7)
N1	C1	C4	123.5(3)	F20	C37	C33	116.2(5)
C2	C1	C4	127.4(3)	F21	C37	C33	109.0(6)
C3	C2	C1	105.1(3)	F19A	C37	C33	108.6(6)
N2	C3	C2	109.6(3)	F21A	C37	C33	120.6(9)
N2	C3	C12	122.1(3)	F21A	C37	F19A	101.0(11)

C2	C3	C12	128.3(3)	F21A	C37	F20A	109.1(10)
C5	C4	C1	121.6(3)	F20A	C37	C33	117.7(7)
C5	C4	C9	119.1(3)	F20A	C37	F19A	95.4(10)
C9	C4	C1	119.1(3)	F22	C38	F24	106.2(5)
C4	C5	C6	120.7(4)	F22	C38	C35	112.3(4)
C5	C6	C10	118.9(4)	F23	C38	F22	107.8(5)
C7	C6	C5	120.7(4)	F23	C38	F24	105.8(4)
C7	C6	C10	120.4(4)	F23	C38	C35	112.9(5)
C6	C7	C8	118.9(4)	F24	C38	C35	111.4(5)
C7	C8	C11	118.3(3)	N5	C39	C40	108.6(3)
C9	C8	C7	120.6(3)	N5	C39	C42	120.5(4)
C9	C8	C11	121.0(4)	C40	C39	C42	130.9(4)
C8	C9	C4	120.0(4)	C39	C40	C41	106.0(4)
F1	C10	C6	111.3(4)	N6	C41	C40	108.5(3)
F2	C10	F1	103.1(4)	N6	C41	C50	122.4(3)
F2	C10	C6	113.6(4)	C40	C41	C50	129.1(4)
F3	C10	F1	103.6(4)	C43	C42	C39	119.9(4)
F3	C10	F2	112.8(4)	C43	C42	C47	119.0(4)
F3	C10	C6	111.7(4)	C47	C42	C39	121.1(4)
F4	C11	C8	111.4(3)	C42	C43	C44	120.4(4)
F5	C11	F4	106.7(3)	C43	C44	C48	117.7(4)
F5	C11	C8	111.9(3)	C45	C44	C43	121.0(4)
F6	C11	F4	106.4(3)	C45	C44	C48	121.2(4)
F6	C11	F5	106.8(3)	C44	C45	C46	118.5(4)
F6	C11	C8	113.2(3)	C45	C46	C47	121.6(4)
C13	C12	C3	119.5(3)	C45	C46	C49	118.0(4)
C13	C12	C17	119.0(4)	C47	C46	C49	120.4(4)
C17	C12	C3	121.4(3)	C42	C47	C46	119.5(4)
C14	C13	C12	120.7(4)	F25	C48	C44	111.3(4)
C13	C14	C15	120.5(4)	F26	C48	F25	106.1(4)
C13	C14	C18	120.6(4)	F26	C48	F27	107.2(4)
C15	C14	C18	118.9(4)	F26	C48	C44	112.3(4)
C16	C15	C14	118.8(4)	F27	C48	F25	106.6(4)
C15	C16	C17	121.3(4)	F27	C48	C44	112.7(4)
C15	C16	C19	120.4(4)	F28	C49	F29	104.2(4)
C17	C16	C19	118.2(4)	F28	C49	C46	111.5(5)
C16	C17	C12	119.7(4)	F29	C49	C46	110.8(5)
F7	C18	F9	105.3(4)	F30	C49	F28	107.3(5)
F7	C18	C14	112.8(4)	F30	C49	F29	109.7(6)
F8	C18	F7	106.9(5)	F30	C49	C46	113.0(4)
F8	C18	F9	107.9(5)	C51	C50	C41	119.9(3)
F8	C18	C14	112.1(4)	C51	C50	C55	118.9(4)
F9	C18	C14	111.4(4)	C55	C50	C41	121.1(4)
F10	C19	F11	105.6(5)	C52	C51	C50	120.5(4)
F10	C19	C16	112.0(4)	C51	C52	C53	120.7(4)
F11	C19	C16	111.8(5)	C51	C52	C56	120.9(4)
F12	C19	F10	107.0(5)	C53	C52	C56	118.4(4)

F12	C19	F11	108.1(5)	C54	C53	C52	118.6(4)
F12	C19	C16	111.9(5)	C53	C54	C57	118.4(4)
N3	C20	C21	108.6(4)	C55	C54	C53	121.3(4)
N3	C20	C23	123.3(3)	C55	C54	C57	120.3(4)
C21	C20	C23	128.0(4)	C54	C55	C50	120.1(4)
C20	C21	C22	106.1(3)	F31	C56	F32	103.5(7)
N4	C22	C21	108.5(4)	F31	C56	F33	110.3(7)
N4	C22	C31	122.5(4)	F31	C56	C52	115.4(7)
C21	C22	C31	128.9(4)	F32	C56	C52	110.6(5)
C24	C23	C20	121.3(4)	F33	C56	F32	99.8(5)
C24	C23	C28	119.0(4)	F33	C56	C52	115.4(5)
C28	C23	C20	119.7(4)	F33A	C56	C52	116.2(8)
C25	C24	C23	120.2(4)	F33A	C56	F32A	109.8(12)
C24	C25	C29	118.5(5)	F33A	C56	F31A	106.7(11)
C26	C25	C24	120.8(4)	F32A	C56	C52	113.3(11)
C26	C25	C29	120.6(5)	F32A	C56	F31A	102.1(10)
C25	C26	C27	119.4(5)	F31A	C56	C52	107.6(7)
C26	C27	C30	120.2(5)	F34	C57	F35	104.9(4)
C28	C27	C26	120.0(5)	F34	C57	F36	106.7(4)
C28	C27	C30	119.7(5)	F34	C57	C54	113.2(4)
C27	C28	C23	120.7(4)	F35	C57	C54	112.9(4)
F13	C29	F14	109.8(9)	F36	C57	F35	105.4(4)
F13	C29	F15	100.1(12)	F36	C57	C54	113.0(3)
F13	C29	C25	118.7(11)				

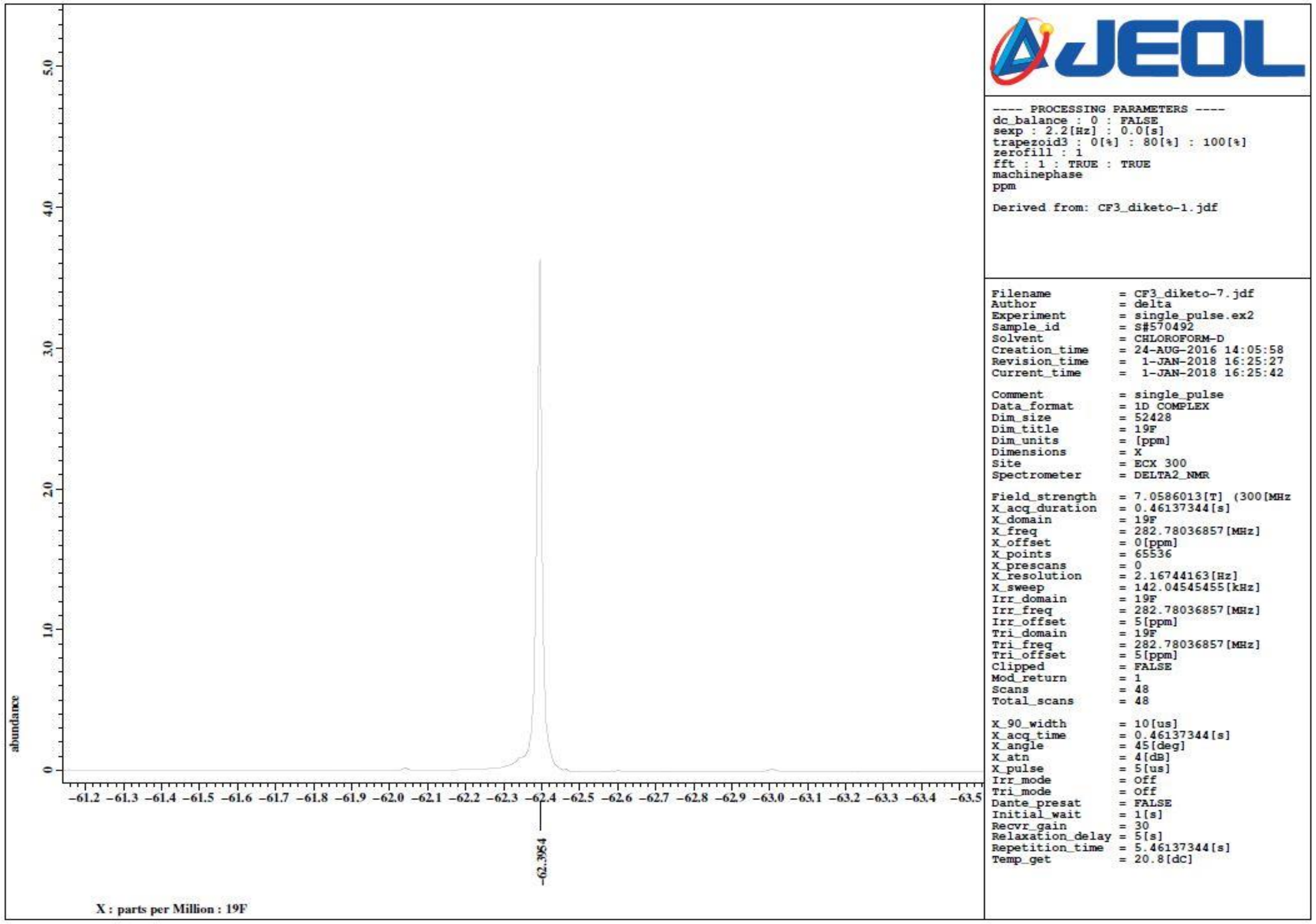
B. SELECTED NMR SPECTRA



```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 0.2[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm

Derived from: Diketone-1.jdf
```

```
Filename           = Diketone-4.jdf
Author             = delta
Experiment         = single_pulse.ex2
Sample_id          = S#765056
Solvent            = CHLOROFORM-D
Creation_time      = 21-DEC-2017 10:22:39
Revision_time      = 21-DEC-2017 09:14:16
Current_time       = 21-DEC-2017 09:14:41

Comment            = single_pulse
Data_format        = 1D COMPLEX
Dim_size           = 26214
Dim_title          = 1H
Dim_units          = [ppm]
Dimensions         = X
Site               = ECA 500
Spectrometer       = JNM-ECA500

Field_strength     = 11.7473579[T] (500[MH
X_acq_duration     = 3.49175808[s]
X_domain           = 1H
X_freq             = 500.15991521[MHz]
X_offset           = 5.0[ppm]
X_points           = 32768
X_prescans         = 0
X_resolution       = 0.28638868[Hz]
X_sweep            = 9.38438438[kHz]
Irr_domain         = 1H
Irr_freq           = 500.15991521[MHz]
Irr_offset         = 5.0[ppm]
Tri_domain         = 1H
Tri_freq           = 500.15991521[MHz]
Tri_offset         = 5.0[ppm]
Clipped            = FALSE
Mod_return         = 1
Scans              = 2
Total_scans        = 2

X_90_width         = 12.54[us]
X_acq_time         = 3.49175808[s]
X_angle            = 45[deg]
X_atn              = 4[dB]
X_pulse            = 6.27[us]
Irr_mode           = Off
Tri_mode           = Off
Dante_presat       = FALSE
Initial_wait       = 1[s]
Recvr_gain         = 50
Relaxation_delay   = 5[s]
Repetition_time    = 8.49175808[s]
Temp_get           = 21.3[dC]
```

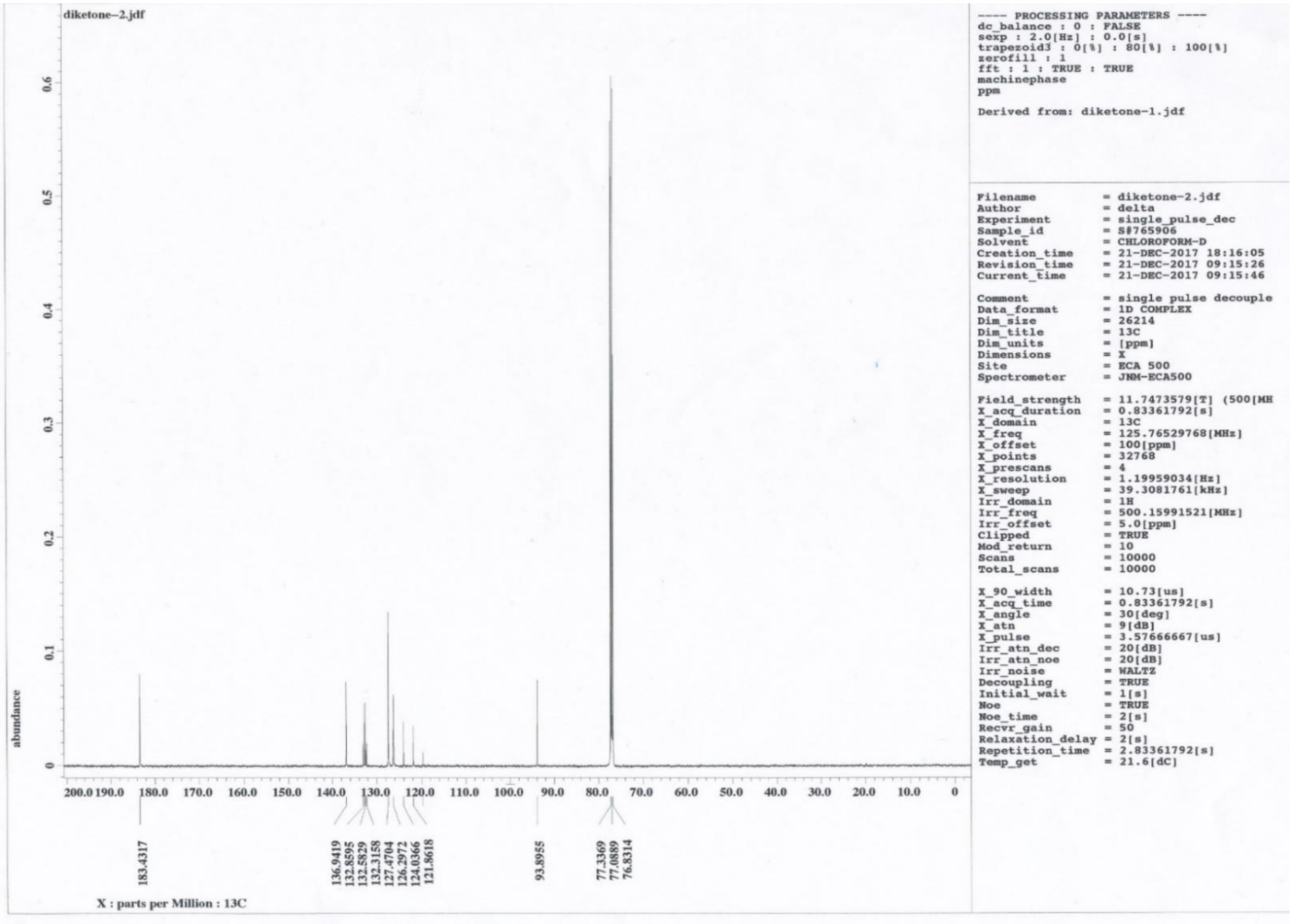
Figure 15. ^{1}H NMR Spectrum of 1,3-bis(3,5-bis(trifluoromethyl)phenyl)-3-hydroxyprop-2-en-1-one.



```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 2.2[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm

Derived from: CF3_diketo-1.jdf
```

```
Filename          = CF3_diketo-7.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = S#570492
Solvent           = CHLOROFORM-D
Creation_time     = 24-AUG-2016 14:05:58
Revision_time     =  1-JAN-2018 16:25:27
Current_time      =  1-JAN-2018 16:25:42

Comment           = single_pulse
Data_format       = 1D COMPLEX
Dim_size          = 52428
Dim_title         = 19F
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 300
Spectrometer      = DELTA2_NMR

Field_strength    = 7.0586013[T] (300[MHz
X_acq_duration    = 0.46137344[s]
X_domain          = 19F
X_freq            = 282.78036857[MHz]
X_offset          = 0[ppm]
X_points          = 65536
X_prescans        = 0
X_resolution      = 2.16744163[Hz]
X_sweep           = 142.04545455[kHz]
Irr_domain        = 19F
Irr_freq          = 282.78036857[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 19F
Tri_freq          = 282.78036857[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 48
Total_scans       = 48

X_90_width        = 10[us]
X_acq_time        = 0.46137344[s]
X_angle           = 45[deg]
X_atn             = 4[dB]
X_pulse           = 5[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 30
Relaxation_delay  = 5[s]
Repetition_time   = 5.46137344[s]
Temp_get          = 20.8[dC]
```

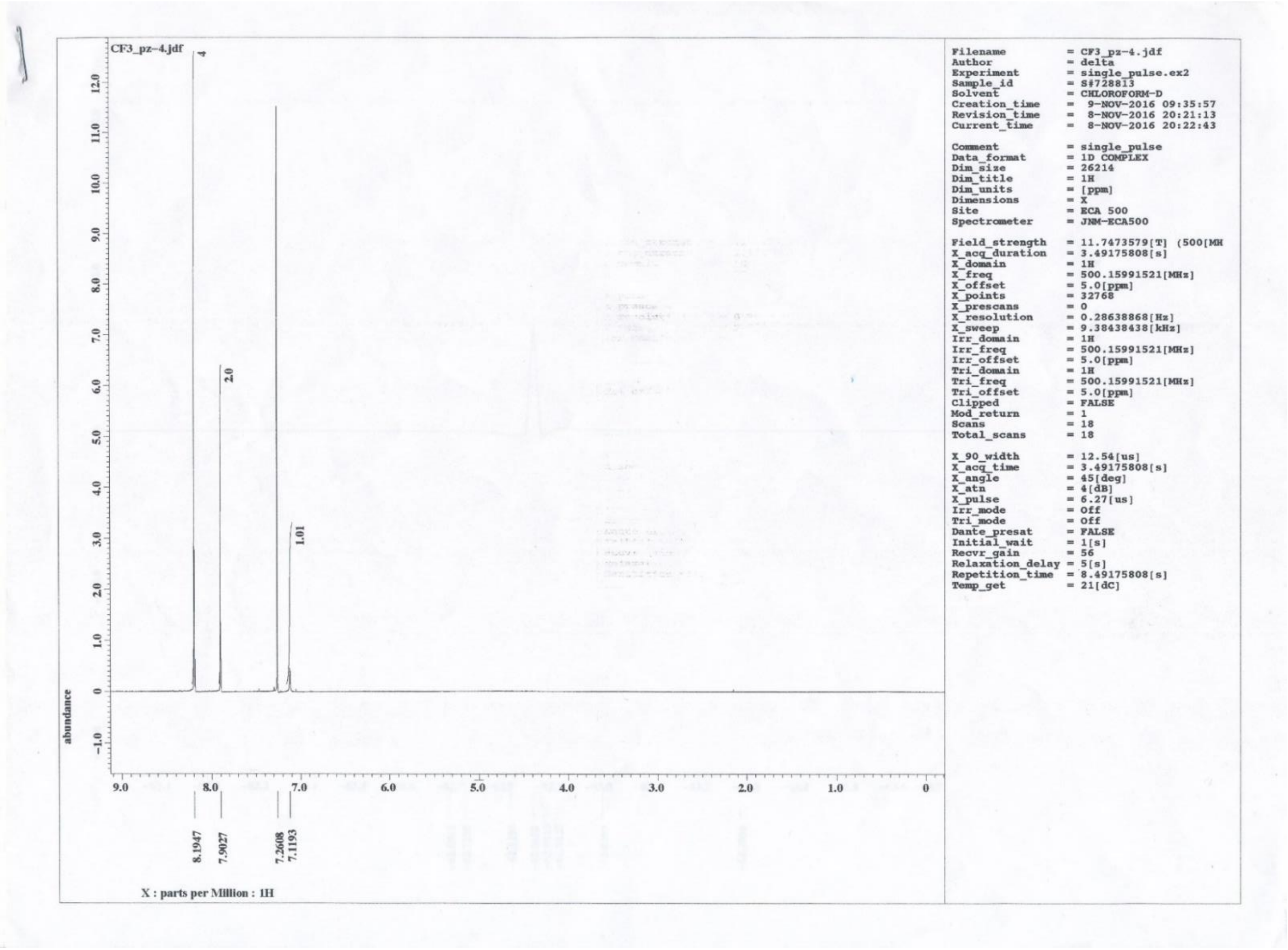
Figure 16. ^{19}F NMR Spectrum of 1,3-bis(3,5-bis(trifluoromethyl)phenyl)-3-hydroxyprop-2-en-1-one.



```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 2.0[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm

Derived from: diketone-1.jdf
```

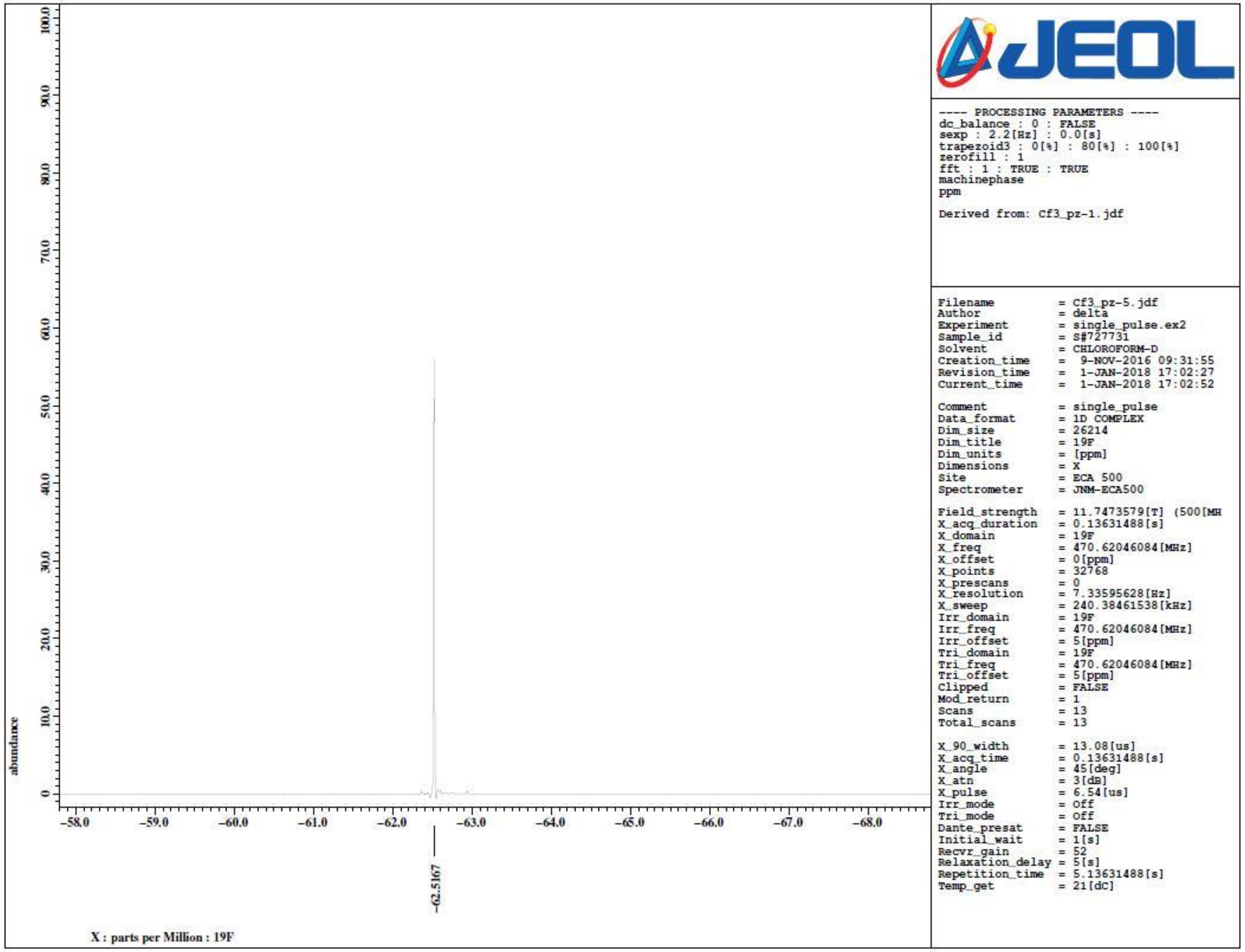
```
Filename          = diketone-2.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#765906
Solvent           = CHLOROFORM-D
Creation_time     = 21-DEC-2017 18:16:05
Revision_time     = 21-DEC-2017 09:15:26
Current_time      = 21-DEC-2017 09:15:46

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 0.83361792[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.19959034[Hz]
X_sweep           = 39.3081761[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Clipped           = TRUE
Mod_return        = 10
Scans             = 10000
Total_scans       = 10000

X_90_width        = 10.73[us]
X_acq_time        = 0.83361792[s]
X_angle           = 30[deg]
X_atn             = 9[dB]
X_pulse           = 3.57666667[us]
Irr_atn_dec       = 20[dB]
Irr_atn_noe       = 20[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 50
Relaxation_delay  = 2[s]
Repetition_time   = 2.83361792[s]
Temp_get          = 21.6[dC]
```

Figure 17. ^{13}C NMR Spectrum of 1,3-bis(3,5-bis(trifluoromethyl)phenyl)-3-hydroxyprop-2-en-1-one.



```
Filename          = CF3_pz-4.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = S#728813
Solvent           = CHLOROFORM-D
Creation_time     =  9-NOV-2016 09:35:57
Revision_time     =  8-NOV-2016 20:21:13
Current_time      =  8-NOV-2016 20:22:43

Comment           = single_pulse
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 3.49175808[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5.0[ppm]
X_points          = 32768
X_prescans        = 0
X_resolution      = 0.28638868[Hz]
X_sweep           = 9.38438438[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Tri_domain        = 1H
Tri_freq          = 500.15991521[MHz]
Tri_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 18
Total_scans       = 18

X_90_width        = 12.54[us]
X_acq_time        = 3.49175808[s]
X_angle           = 45[deg]
X_atn             = 4[dB]
X_pulse           = 6.27[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 56
Relaxation_delay  = 5[s]
Repetition_time   = 8.49175808[s]
Temp_get          = 21[dC]
```

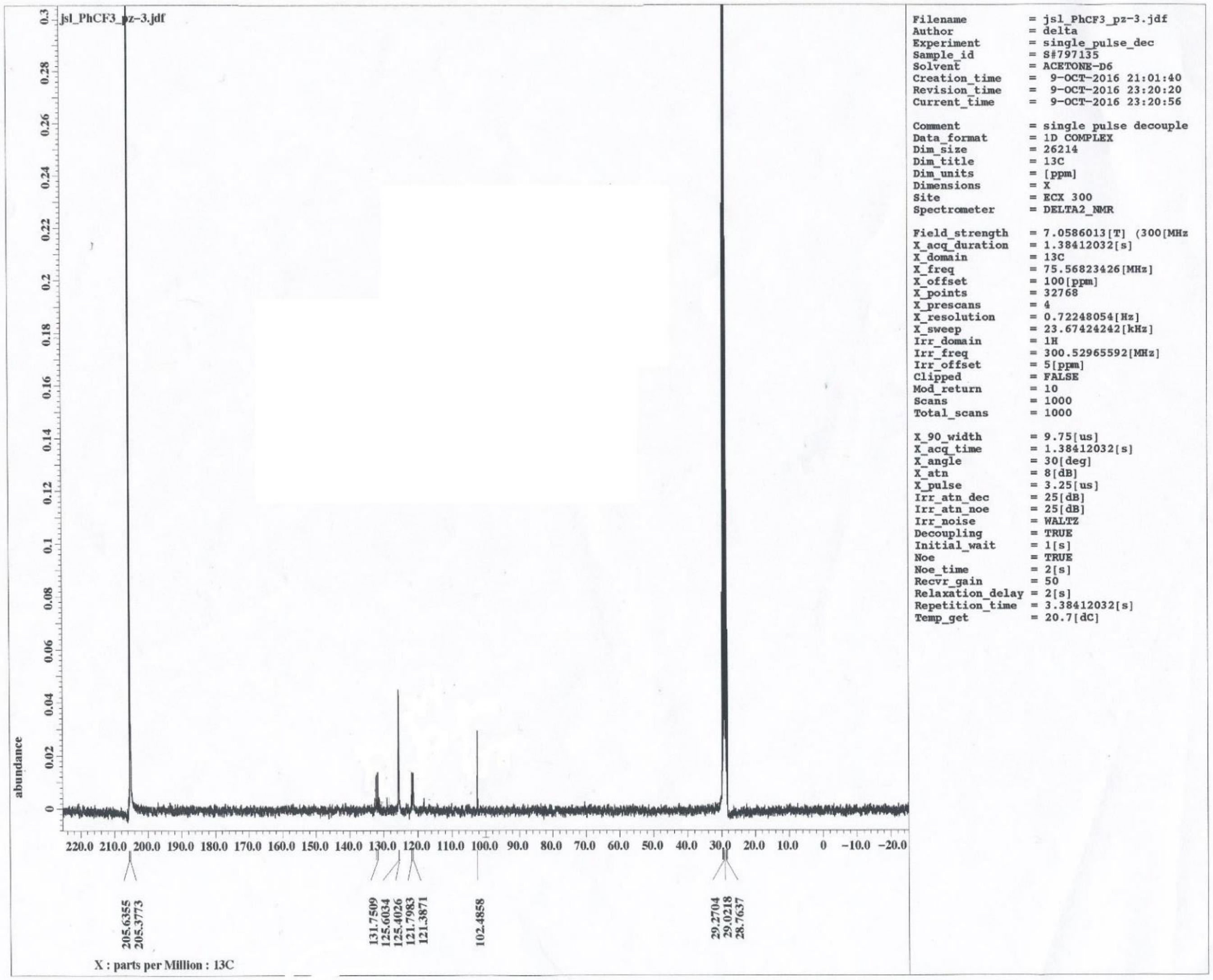
Figure 18. ^{1}H NMR Spectrum of [3,5-(3,5-$(CF_3)_2$Ph)$_2$PzH].



```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 2.2[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm

Derived from: Cf3_pz-1.jdf
```

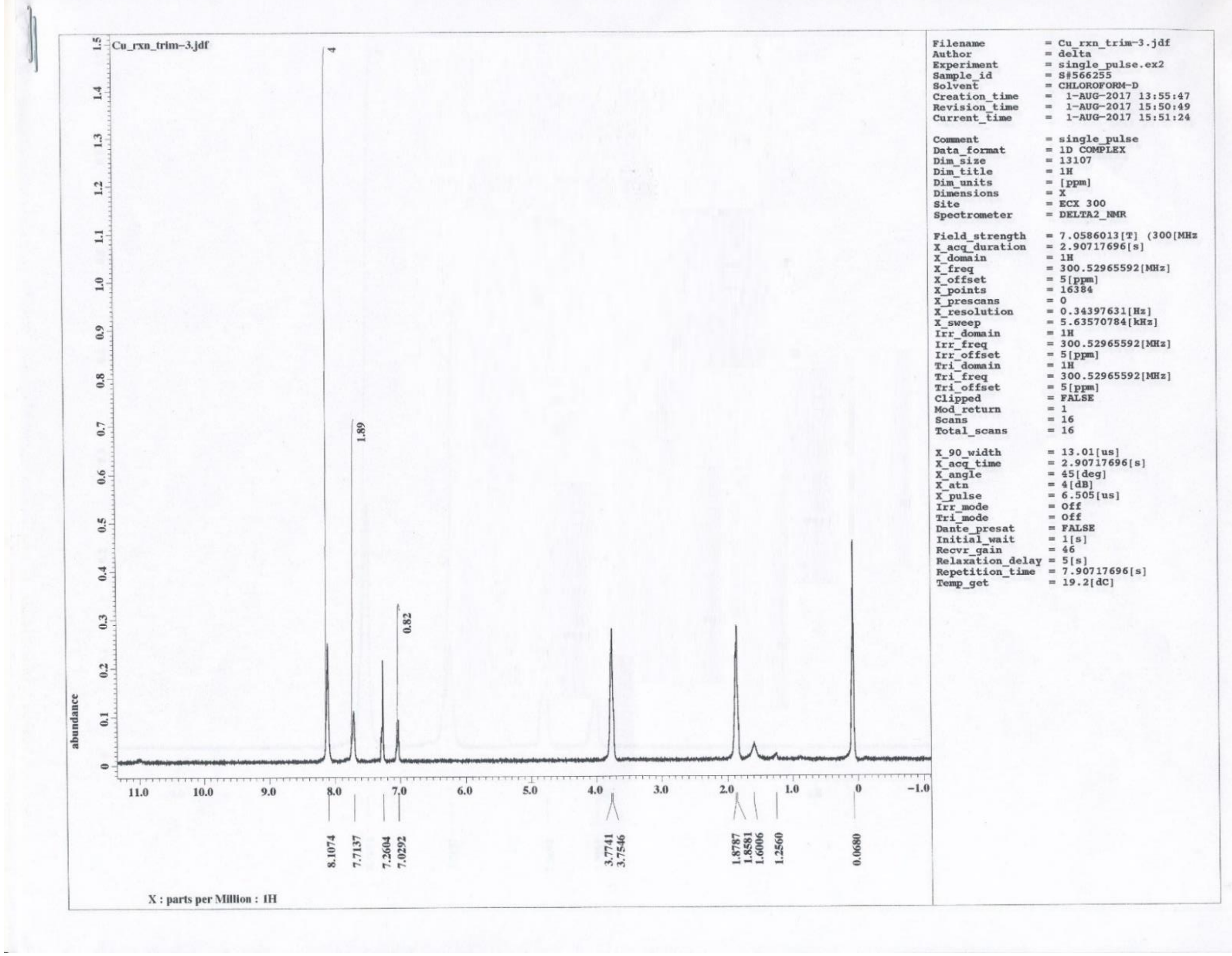
```
Filename          = Cf3_pz-5.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = S#727731
Solvent           = CHLOROFORM-D
Creation_time     =  9-NOV-2016 09:31:55
Revision_time     =  1-JAN-2018 17:02:27
Current_time      =  1-JAN-2018 17:02:52

Comment           = single_pulse
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 19F
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 0.13631488[s]
X_domain          = 19F
X_freq            = 470.62046084[MHz]
X_offset          = 0[ppm]
X_points          = 32768
X_prescans        = 0
X_resolution      = 7.33595628[Hz]
X_sweep           = 240.38461538[kHz]
Irr_domain        = 19F
Irr_freq          = 470.62046084[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 19F
Tri_freq          = 470.62046084[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 13
Total_scans       = 13

X_90_width        = 13.08[us]
X_acq_time        = 0.13631488[s]
X_angle           = 45[deg]
X_atn             = 3[dB]
X_pulse           = 6.54[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 52
Relaxation_delay  = 5[s]
Repetition_time   = 5.13631488[s]
Temp_get          = 21[dC]
```

Figure 19. ^{19}F NMR Spectrum of [3,5-(3,5-$(CF_3)_2$Ph$)_2$PzH].



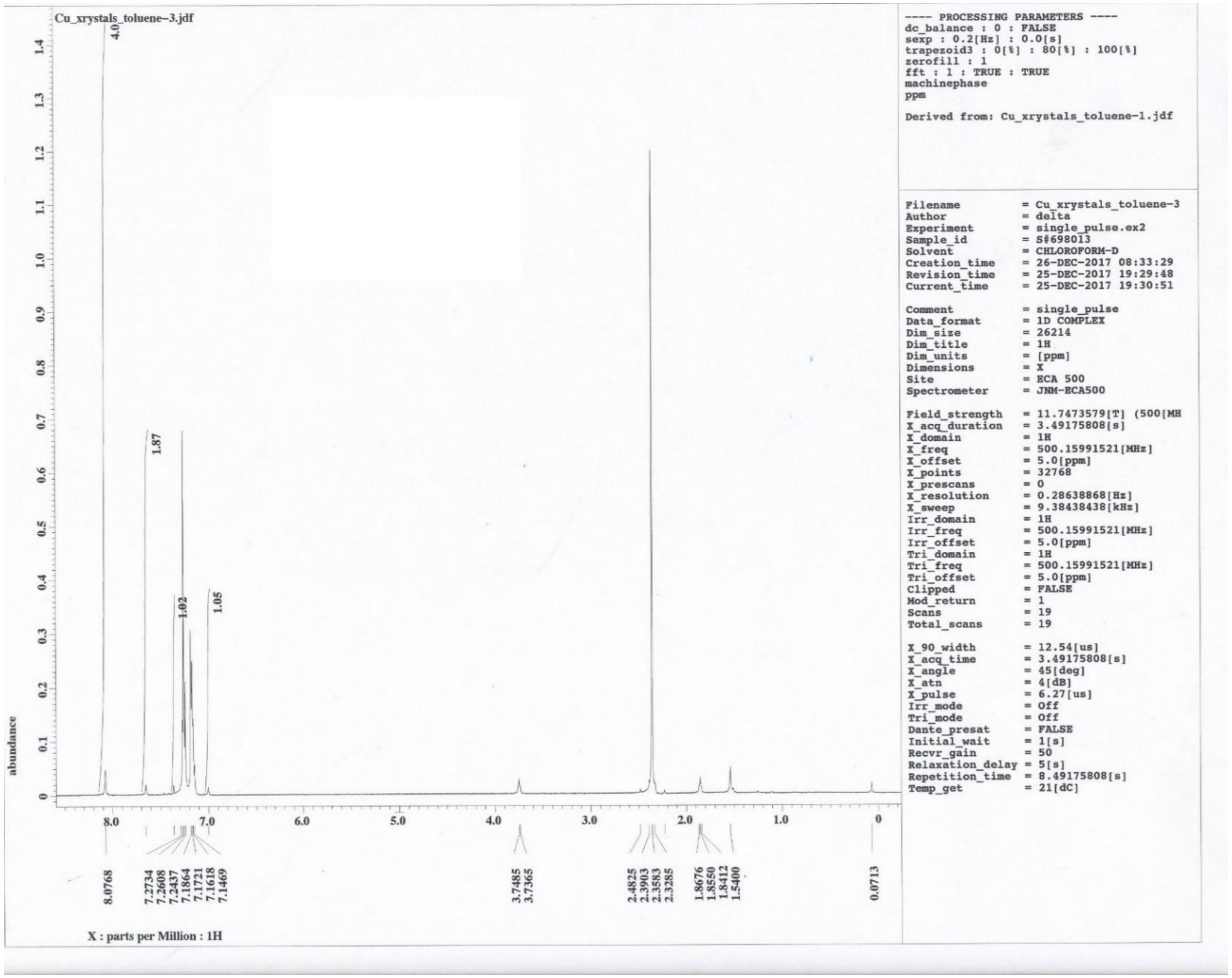
```
Filename          = jsl_PhCF3_pz-3.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#797135
Solvent           = ACETONE-D6
Creation_time     =  9-OCT-2016 21:01:40
Revision_time     =  9-OCT-2016 23:20:20
Current_time      =  9-OCT-2016 23:20:56

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 300
Spectrometer      = DELTA2_NMR

Field_strength    = 7.0586013[T] (300[MHz
X_acq_duration    = 1.38412032[s]
X_domain          = 13C
X_freq            = 75.56823426[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 0.72248054[Hz]
X_sweep           = 23.67424242[kHz]
Irr_domain        = 1H
Irr_freq          = 300.52965592[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 10
Scans             = 1000
Total_scans       = 1000

X_90_width        = 9.75[us]
X_acq_time        = 1.38412032[s]
X_angle           = 30[deg]
X_atn             = 8[dB]
X_pulse           = 3.25[us]
Irr_atn_dec       = 25[dB]
Irr_atn_noe       = 25[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 50
Relaxation_delay  = 2[s]
Repetition_time   = 3.38412032[s]
Temp_get          = 20.7[dC]
```

Figure 20. ^{13}C NMR Spectrum of [3,5-(3,5-$(CF_3)_2$Ph$)_2$PzH].



```
Filename          = Cu_rxn_trim-3.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = S#566255
Solvent           = CHLOROFORM-D
Creation_time     =  1-AUG-2017 13:55:47
Revision_time     =  1-AUG-2017 15:50:49
Current_time      =  1-AUG-2017 15:51:24

Comment           = single_pulse
Data_format       = 1D COMPLEX
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 300
Spectrometer      = DELTA2_NMR

Field_strength    = 7.0586013[T] (300[MHz
X_acq_duration    = 2.90717696[s]
X_domain          = 1H
X_freq            = 300.52965592[MHz]
X_offset          = 5[ppm]
X_points          = 16384
X_prescans        = 0
X_resolution      = 0.34397631[Hz]
X_sweep           = 5.63570784[kHz]
Irr_domain        = 1H
Irr_freq          = 300.52965592[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 300.52965592[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 16
Total_scans       = 16

X_90_width        = 13.01[us]
X_acq_time        = 2.90717696[s]
X_angle           = 45[deg]
X_atn             = 4[dB]
X_pulse           = 6.505[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 46
Relaxation_delay  = 5[s]
Repetition_time   = 7.90717696[s]
Temp_get          = 19.2[dC]
```

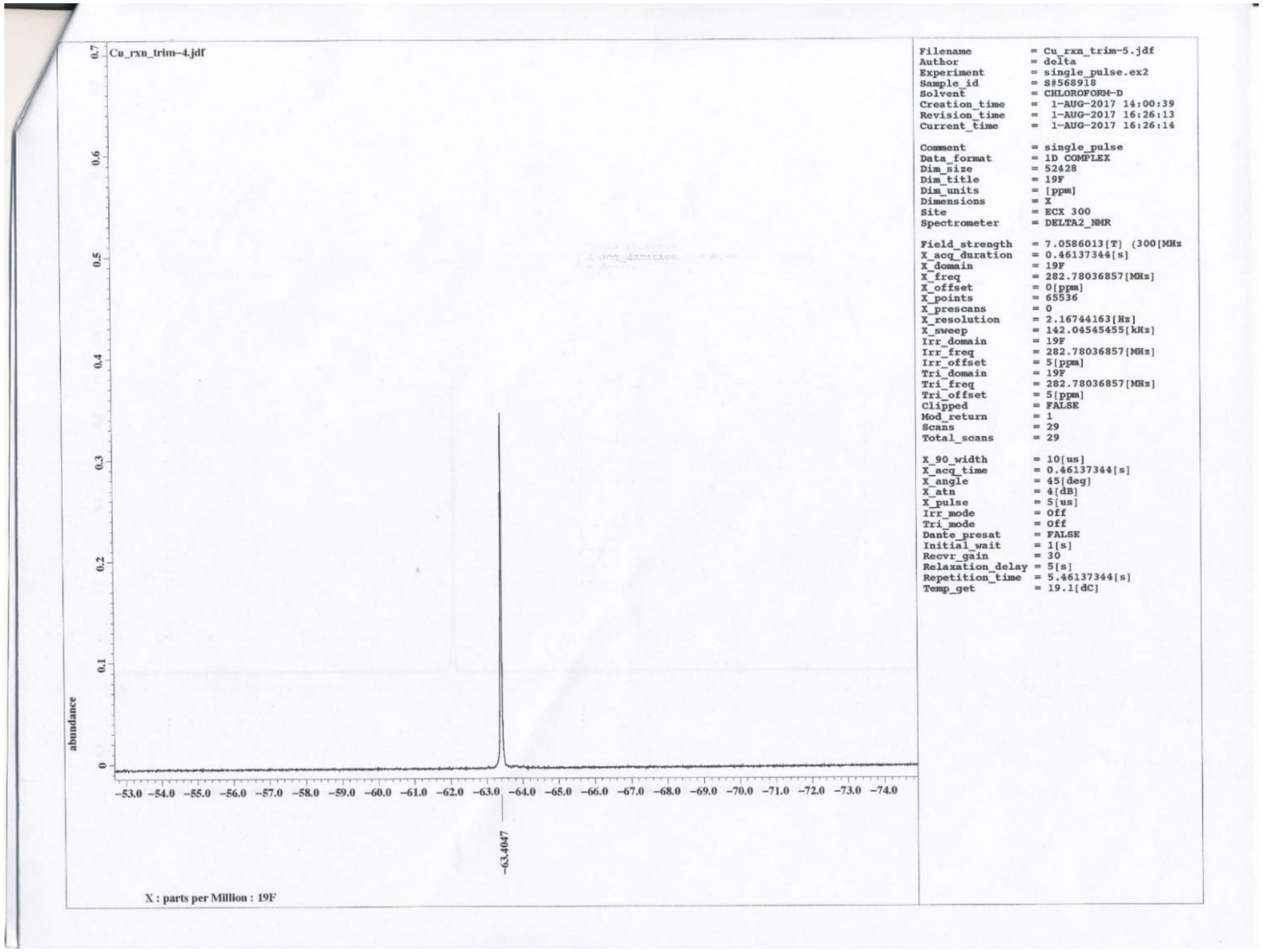
Figure 21. ^{1}H NMR Spectrum of $\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]Cu\}_3$



```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 0.2[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm

Derived from: Cu_xrystals_toluene-1.jdf
```

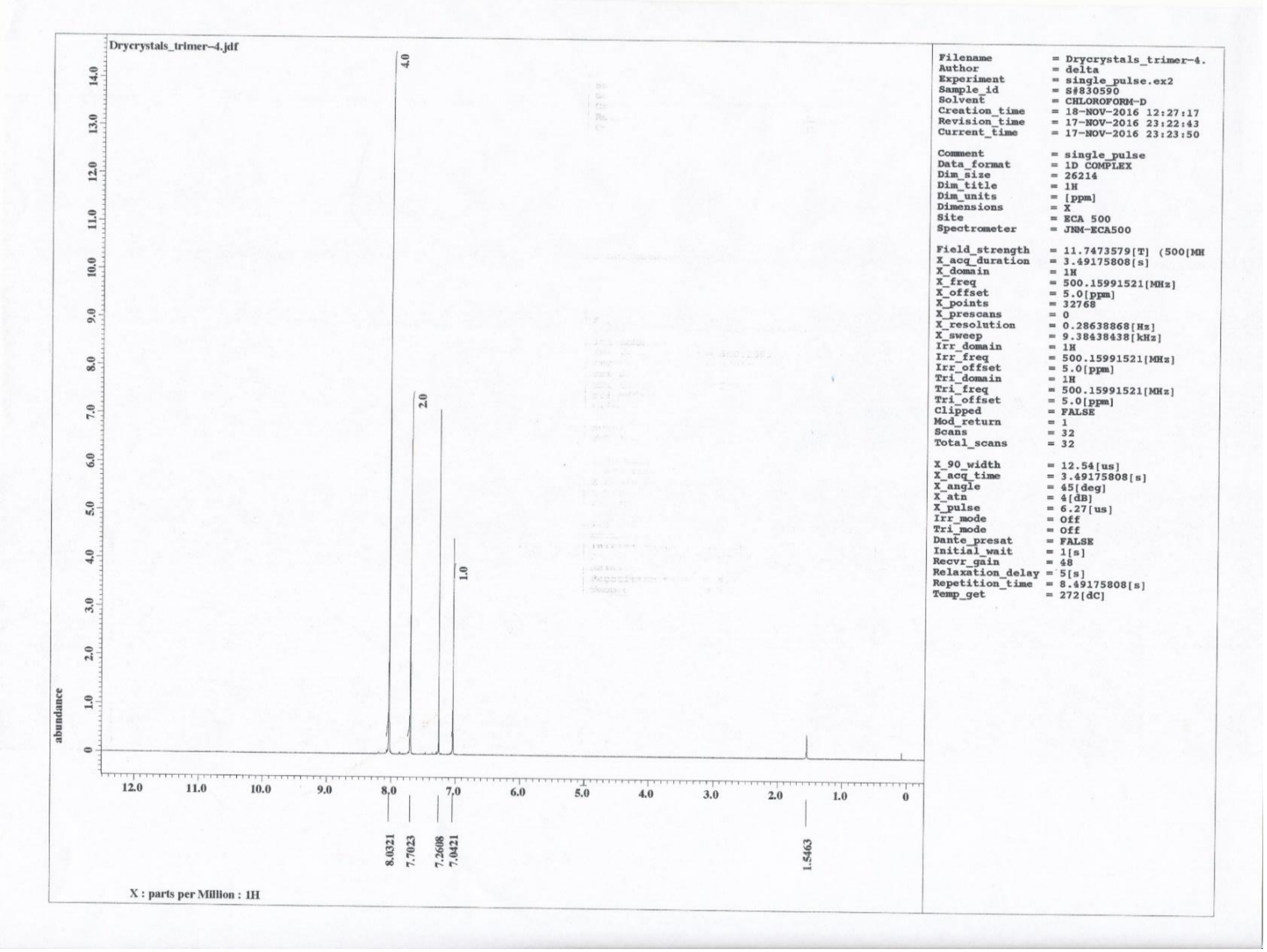
```
Filename          = Cu_xrystals_toluene-3
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = S#698013
Solvent           = CHLOROFORM-D
Creation_time     = 26-DEC-2017 08:33:29
Revision_time     = 25-DEC-2017 19:29:48
Current_time      = 25-DEC-2017 19:30:51

Comment           = single_pulse
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 3.49175808[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5.0[ppm]
X_points          = 32768
X_prescans        = 0
X_resolution      = 0.28638868[Hz]
X_sweep           = 9.38438438[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Tri_domain        = 1H
Tri_freq          = 500.15991521[MHz]
Tri_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 19
Total_scans       = 19

X_90_width        = 12.54[us]
X_acq_time        = 3.49175808[s]
X_angle           = 45[deg]
X_atn             = 4[dB]
X_pulse           = 6.27[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 50
Relaxation_delay  = 5[s]
Repetition_time   = 8.49175808[s]
Temp_get          = 21[dC]
```

Figure 22. ^{1}H NMR Spectrum of {[3,5-(3,5-$(CF_3)_2$Ph)$_2$Pz]Cu}$_3$. C_7H_8



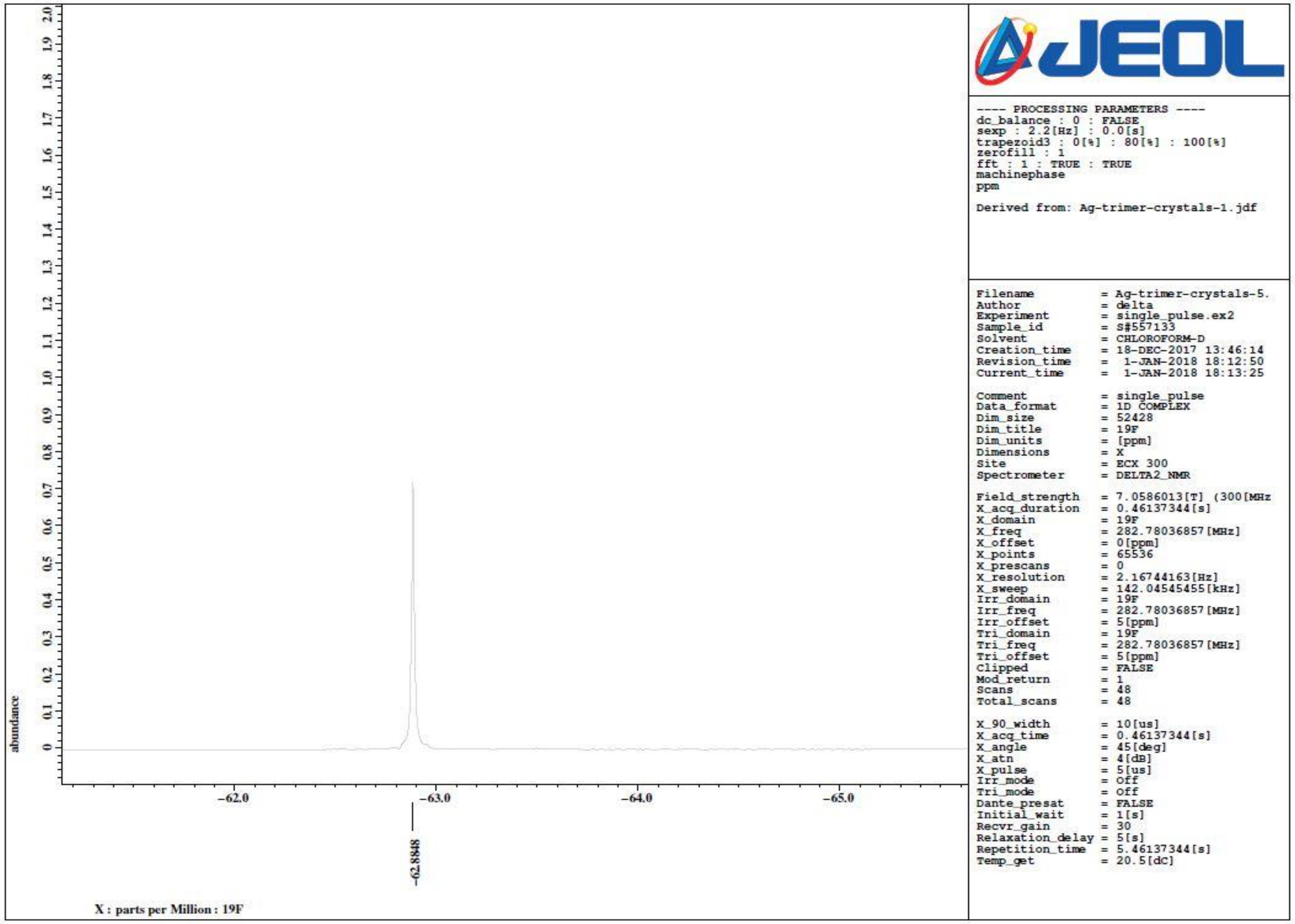
```
Filename          = Cu_rxn_trim-5.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = S#568918
Solvent           = CHLOROFORM-D
Creation_time     =  1-AUG-2017 14:00:39
Revision_time     =  1-AUG-2017 16:26:13
Current_time      =  1-AUG-2017 16:26:14

Comment           = single_pulse
Data_format       = 1D COMPLEX
Dim_size          = 52428
Dim_title         = 19F
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 300
Spectrometer      = DELTA2_NMR

Field_strength    = 7.0586013[T] (300[MHz
X_acq_duration    = 0.46137344[s]
X_domain          = 19F
X_freq            = 282.78036857[MHz]
X_offset          = 0[ppm]
X_points          = 65536
X_prescans        = 0
X_resolution      = 2.16744163[Hz]
X_sweep           = 142.04545455[kHz]
Irr_domain        = 19F
Irr_freq          = 282.78036857[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 19F
Tri_freq          = 282.78036857[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 29
Total_scans       = 29

X_90_width        = 10[us]
X_acq_time        = 0.46137344[s]
X_angle           = 45[deg]
X_atn             = 4[dB]
X_pulse           = 5[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 30
Relaxation_delay  = 5[s]
Repetition_time   = 5.46137344[s]
Temp_get          = 19.1[dC]
```

Figure 23. ^{19}F NMR Spectrum of $\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]Cu\}_3$.



```
Filename            = Drycrystals_trimer-4.
Author              = delta
Experiment          = single_pulse.ex2
Sample_id           = S#830590
Solvent             = CHLOROFORM-D
Creation_time       = 18-NOV-2016 12:27:17
Revision_time       = 17-NOV-2016 23:22:43
Current_time        = 17-NOV-2016 23:23:50

Comment             = single_pulse
Data_format         = 1D COMPLEX
Dim_size            = 26214
Dim_title           = 1H
Dim_units           = [ppm]
Dimensions          = X
Site                = ECA 500
Spectrometer        = JNM-ECA500

Field_strength      = 11.7473579[T] (500[MH
X_acq_duration      = 3.49175808[s]
X_domain            = 1H
X_freq              = 500.15991521[MHz]
X_offset            = 5.0[ppm]
X_points            = 32768
X_prescans          = 0
X_resolution        = 0.28638868[Hz]
X_sweep             = 9.38438438[kHz]
Irr_domain          = 1H
Irr_freq            = 500.15991521[MHz]
Irr_offset          = 5.0[ppm]
Tri_domain          = 1H
Tri_freq            = 500.15991521[MHz]
Tri_offset          = 5.0[ppm]
Clipped             = FALSE
Mod_return          = 1
Scans               = 32
Total_scans         = 32

X_90_width          = 12.54[us]
X_acq_time          = 3.49175808[s]
X_angle             = 45[deg]
X_atn               = 4[dB]
X_pulse             = 6.27[us]
Irr_mode            = Off
Tri_mode            = Off
Dante_presat        = FALSE
Initial_wait        = 1[s]
Recvr_gain          = 48
Relaxation_delay    = 5[s]
Repetition_time     = 8.49175808[s]
Temp_get            = 272[dC]
```

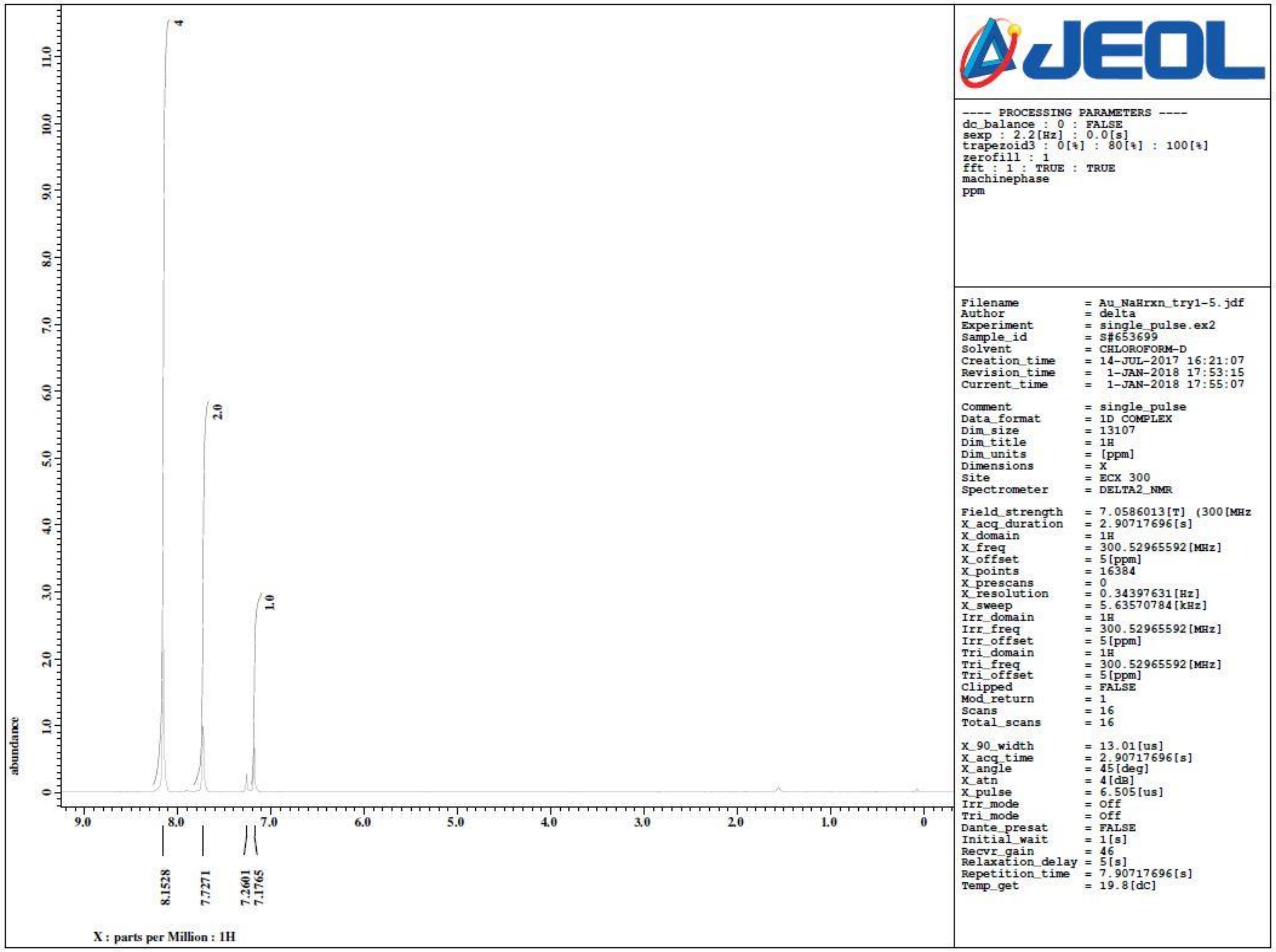
Figure 24. ^{1}H NMR Spectrum of $\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]Ag\}_3$.



```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 2.2[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm

Derived from: Ag-trimer-crystals-1.jdf
```

```
Filename           = Ag-trimer-crystals-5.
Author             = delta
Experiment         = single_pulse.ex2
Sample_id          = S#557133
Solvent            = CHLOROFORM-D
Creation_time      = 18-DEC-2017 13:46:14
Revision_time      =  1-JAN-2018 18:12:50
Current_time       =  1-JAN-2018 18:13:25

Comment            = single_pulse
Data_format        = 1D COMPLEX
Dim_size           = 52428
Dim_title          = 19F
Dim_units          = [ppm]
Dimensions         = X
Site               = ECX 300
Spectrometer       = DELTA2_NMR

Field_strength     = 7.0586013[T] (300[MHz
X_acq_duration     = 0.46137344[s]
X_domain           = 19F
X_freq             = 282.78036857[MHz]
X_offset           = 0[ppm]
X_points           = 65536
X_prescans         = 0
X_resolution       = 2.16744163[Hz]
X_sweep            = 142.04545455[kHz]
Irr_domain         = 19F
Irr_freq           = 282.78036857[MHz]
Irr_offset         = 5[ppm]
Tri_domain         = 19F
Tri_freq           = 282.78036857[MHz]
Tri_offset         = 5[ppm]
Clipped            = FALSE
Mod_return         = 1
Scans              = 48
Total_scans        = 48

X_90_width         = 10[us]
X_acq_time         = 0.46137344[s]
X_angle            = 45[deg]
X_atn              = 4[dB]
X_pulse            = 5[us]
Irr_mode           = Off
Tri_mode           = Off
Dante_presat       = FALSE
Initial_wait       = 1[s]
Recvr_gain         = 30
Relaxation_delay = 5[s]
Repetition_time    = 5.46137344[s]
Temp_get           = 20.5[dC]
```

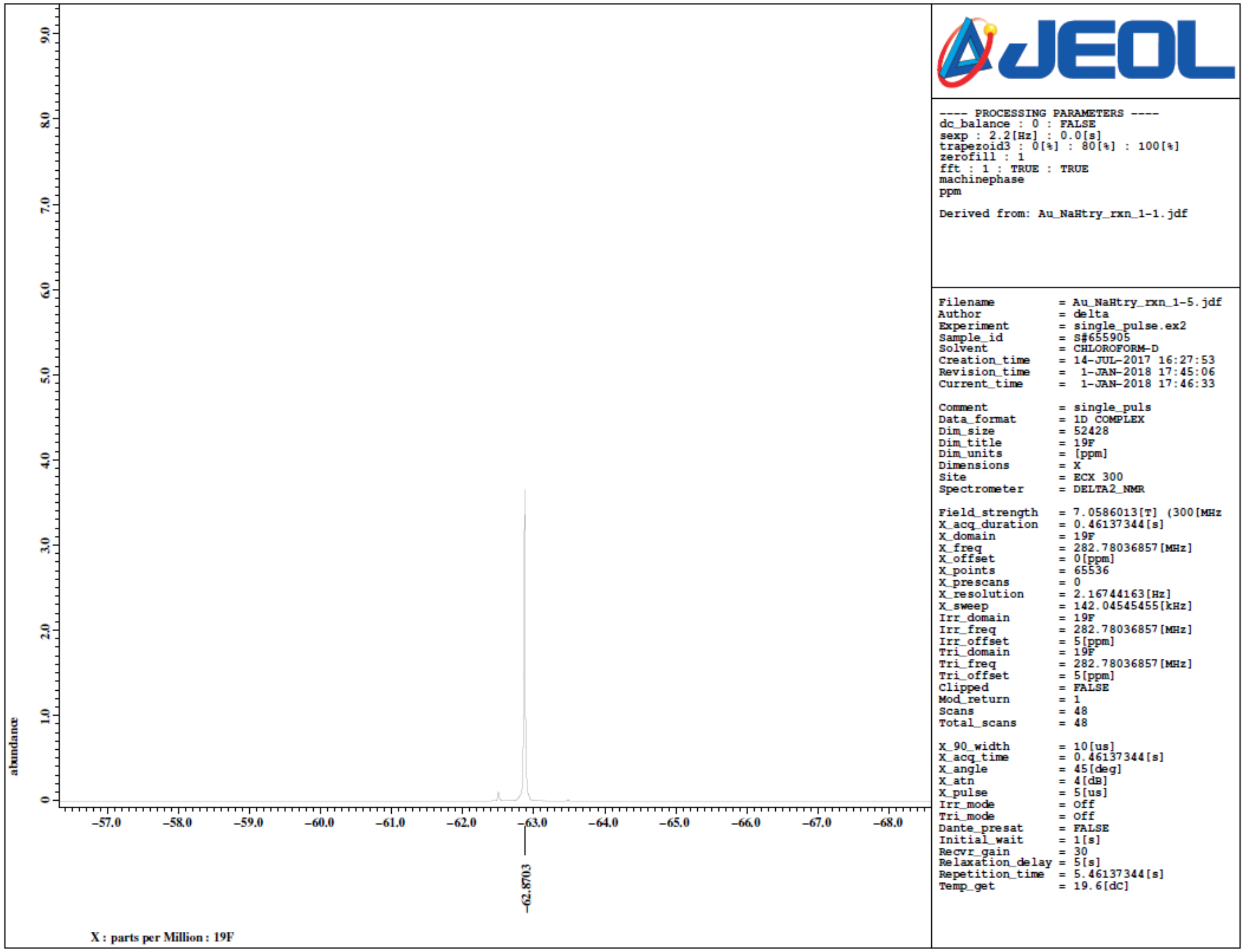
Figure 25. ^{19}F NMR Spectrum of {[3,5-(3,5-(CF$_3$)$_2$Ph)$_2$Pz]Ag}$_3$



```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 2.2[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm
```

```
Filename          = Au_NaHrxn_try1-5.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = S#653699
Solvent           = CHLOROFORM-D
Creation_time     = 14-JUL-2017 16:21:07
Revision_time     =  1-JAN-2018 17:53:15
Current_time      =  1-JAN-2018 17:55:07

Comment           = single_pulse
Data_format       = 1D COMPLEX
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 300
Spectrometer      = DELTA2_NMR

Field_strength    = 7.0586013[T] (300[MHz
X_acq_duration    = 2.90717696[s]
X_domain          = 1H
X_freq            = 300.52965592[MHz]
X_offset          = 5[ppm]
X_points          = 16384
X_prescans        = 0
X_resolution      = 0.34397631[Hz]
X_sweep           = 5.63570784[kHz]
Irr_domain        = 1H
Irr_freq          = 300.52965592[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 300.52965592[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 16
Total_scans       = 16

X_90_width        = 13.01[us]
X_acq_time        = 2.90717696[s]
X_angle           = 45[deg]
X_atn             = 4[dB]
X_pulse           = 6.505[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 46
Relaxation_delay  = 5[s]
Repetition_time   = 7.90717696[s]
Temp_get          = 19.8[dC]
```

Figure 26. ^{1}H NMR Spectrum of {[3,5-(3,5-$(CF_3)_2$Ph)$_2$Pz]Au}$_3$

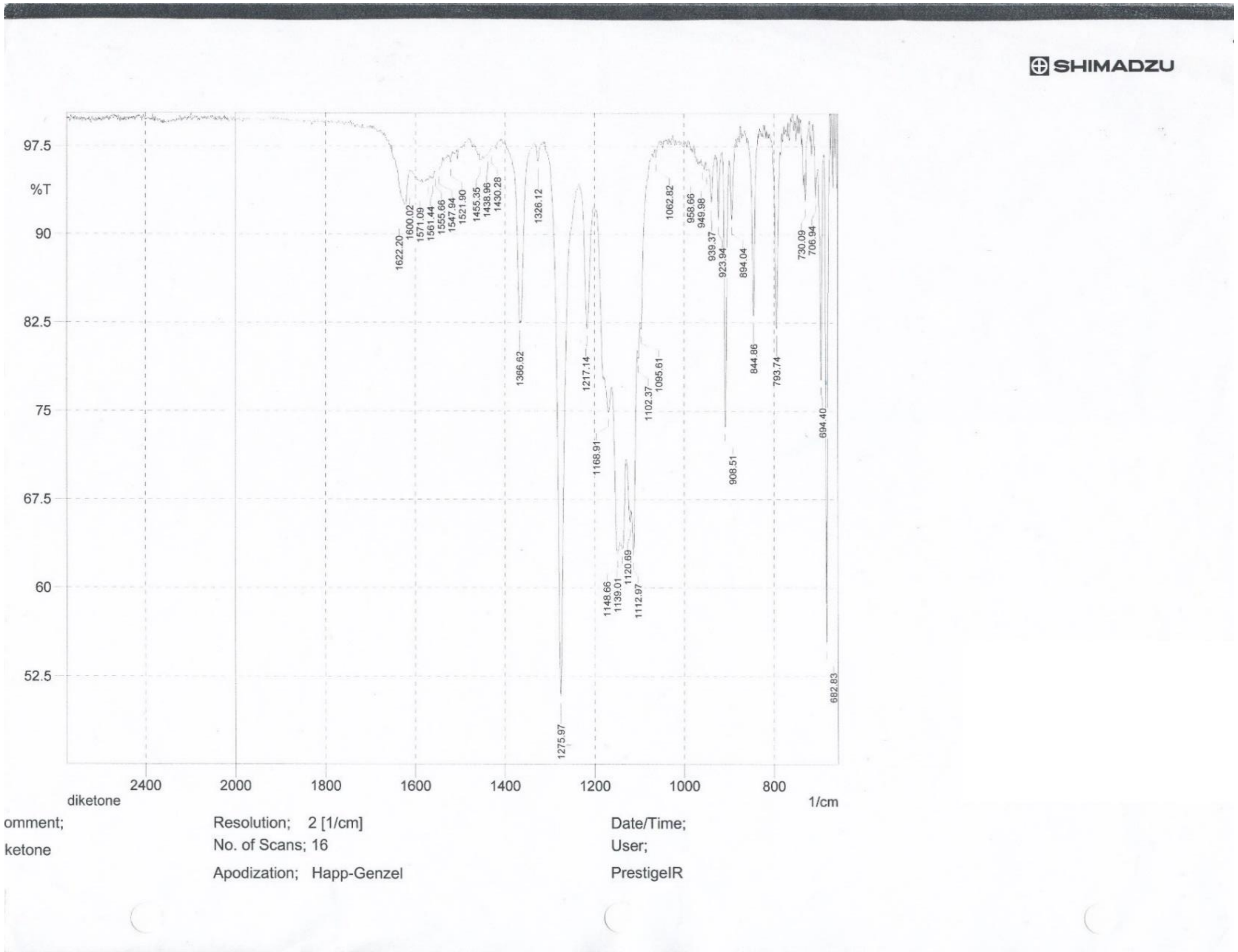


```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 2.2[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm

Derived from: Au_NaHtry_rxn_1-1.jdf
```

```
Filename          = Au_NaHtry_rxn_1-5.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = S#655905
Solvent           = CHLOROFORM-D
Creation_time     = 14-JUL-2017 16:27:53
Revision_time     =  1-JAN-2018 17:45:06
Current_time      =  1-JAN-2018 17:46:33

Comment           = single_puls
Data_format       = 1D COMPLEX
Dim_size          = 52428
Dim_title         = 19F
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 300
Spectrometer      = DELTA2_NMR

Field_strength    = 7.0586013[T] (300[MHz
X_acq_duration    = 0.46137344[s]
X_domain          = 19F
X_freq            = 282.78036857[MHz]
X_offset          = 0[ppm]
X_points          = 65536
X_prescans        = 0
X_resolution      = 2.16744163[Hz]
X_sweep           = 142.04545455[kHz]
Irr_domain        = 19F
Irr_freq          = 282.78036857[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 19F
Tri_freq          = 282.78036857[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 48
Total_scans       = 48

X_90_width        = 10[us]
X_acq_time        = 0.46137344[s]
X_angle           = 45[deg]
X_atn             = 4[dB]
X_pulse           = 5[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 30
Relaxation_delay  = 5[s]
Repetition_time   = 5.46137344[s]
Temp_get          = 19.6[dC]
```

Figure 27. ^{19}F NMR Spectrum of {[3,5-(3,5-(CF$_3$)$_2$Ph)$_2$Pz]Au}$_3$.

C. SELECTED INFRARED SPECTRA

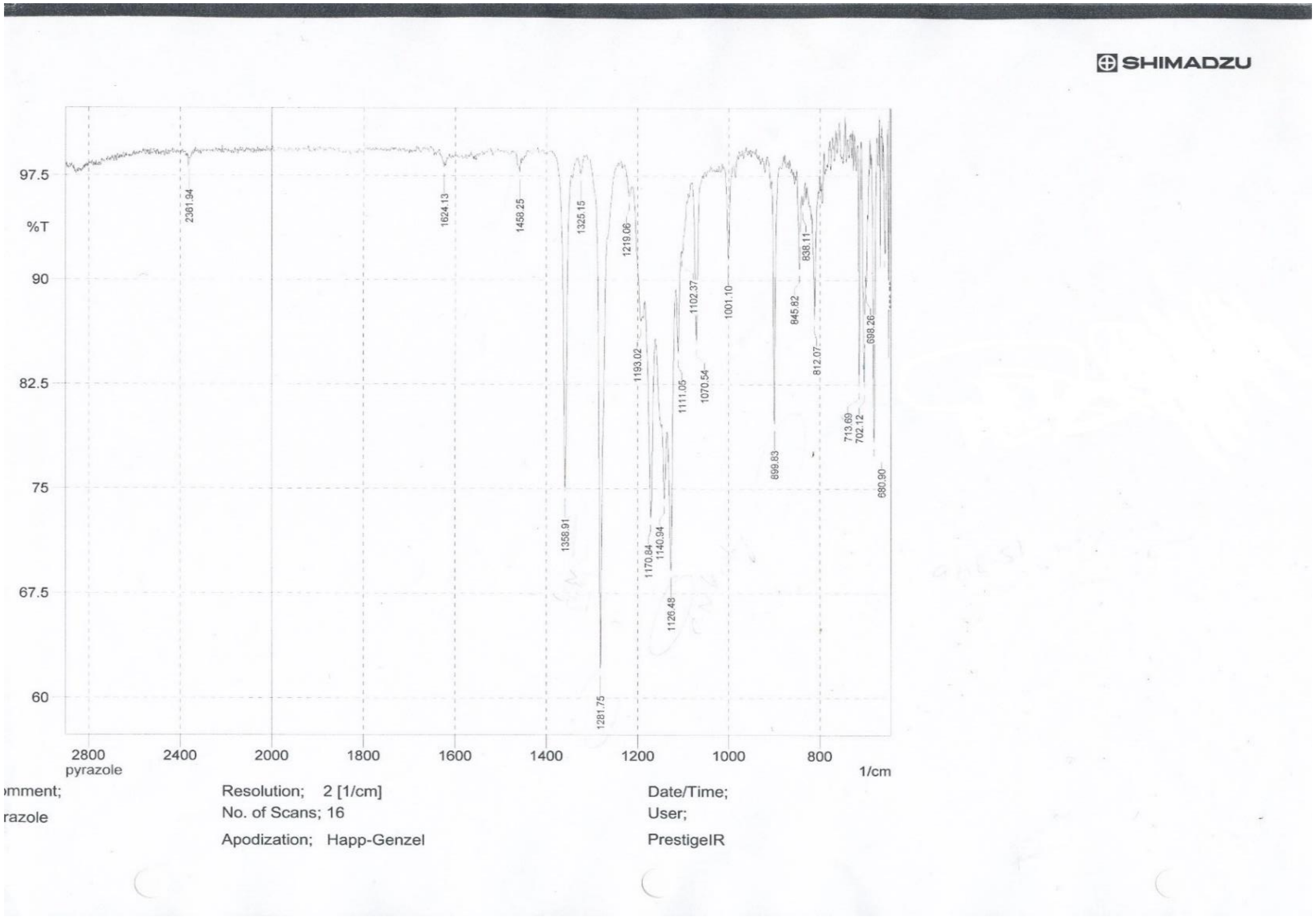


omment;
ketone

Resolution; 2 [1/cm]
No. of Scans; 16
Apodization; Happ-Genzel

Date/Time;
User;
PrestigeIR

Figure 28. Infrared Spectrum of 1,3-bis(3,5-bis(trifluoromethyl)phenyl)-3-hydroxyprop-2-en-1-one.



mment;
razole

Resolution; 2 [1/cm]
No. of Scans; 16
Apodization; Happ-Genzel

Date/Time;
User;
PrestigeIR

Figure 29. Infrared spectrum of [3,5-(3,5-$(CF_3)_2$Ph$)_2$PzH].

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