Electronic Supplementary Information

Constructing deep-blue bis-tridentate Ir(III) phosphors with fluorene-based dianionic chelates

Ze-Lin Zhu,[a] Wen-Cheng Chen,[a,b] Shao-Fei Ni,[c] Jie Yan,[d] Sheng Fu Wang,[e] Li-Wen Fu,[e] Han-Yan Tsai,[e] Yun Chi[a,d,e,*] and Chun-Sing Lee[a,*]

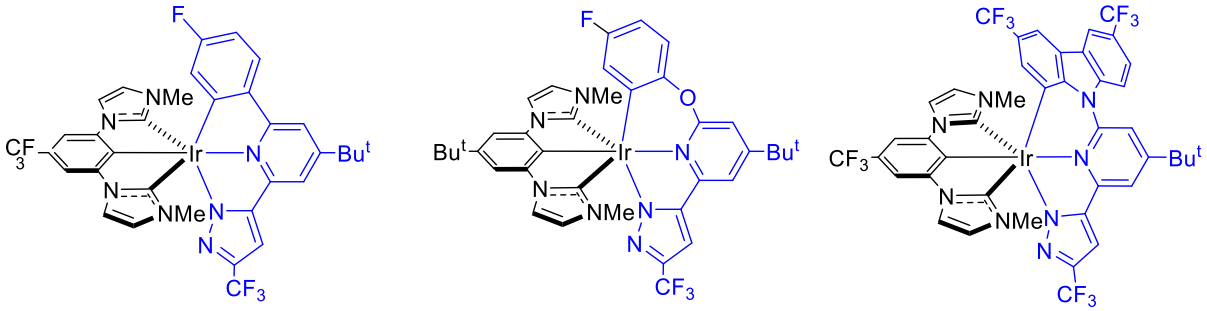
[a] Center of Super-Diamond and Advanced Films (COSDAF) and Department of Chemistry City University of Hong Kong, Hong Kong SAR, China, E-mail: apcslee@cityu.edu.hk.

[b] School of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou, 510006, China

[c] Department of Chemistry and Key Laboratory for Preparation and Application of Ordered Structural Materials of Guangdong Province, Shantou University, Shantou, Guangdong 515063, P.R. China.

[d] Department of Materials Science and Engineering, City University of Hong Kong, Hong Kong SAR, China, E-mail: yunchi@cityu.edu.hk

[e] Department of Chemistry and Frontier Research Center on Fundamental and Applied Sciences of Matters, National Tsing Hua University, Hsinchu 30013, Taiwan.



[Ir(mimb)(pzy^{tB}ph^{F})] (**SB**) [Ir(mimb)(pzy^{tB}Px^{F})] (**Px-5**) [Ir(mimf)(pzy^{tB}Cz^{F6})] (**Cz-2**)

Scheme S1. Chemical structure of bis-tridentate Ir(III) phosphors **SB**, **Px-5**, and **Cz-2**.

General information:

All reactions were conducted under N_2 atmosphere and solvents were dried prior to use. Commercially available reagents were used without further purification. ^{1}H and ^{19}F NMR spectra were measured with Varian Mercury-400 instrument or Varian Mercury-500 instrument. Elemental analysis was carried out on a Heraeus CHN-O Rapid Elementary Analyzer. Mass spectra were recorded on a JEOL Model: JMS-T200GC AccuTOF GCx instrument operating in electron impact (EI) or field desorption (FD) mode. All chemicals were purchased from commercial resources and used without further purification.

According to Fermi's golden role, the rate of phosphorescence is given by

$$k_p \propto \sum_i \left| \frac{\langle\, {}^1\psi_i | H_{SOC} |\, {}^3\psi_1 \rangle}{E(T_1) - E(S_i)} \right|^2 \langle\, {}^1\psi_i | e\vec{r} |\, {}^1\psi_0 \rangle \qquad (1)$$

where $E(T_1)$ and $E(S_i)$ is the energy of first excited triplet and i-th singlet manifold, respectively. ${}^3\psi_1$, ${}^1\psi_i$, ${}^1\psi_0$ are the wavefunctions of the first excited triplet, i-th and ground singlet manifold, respectively, $|H_{SOC}|$ is the Hamiltonian of the SOC (spin-orbital coupling) perturbation. Thus, it is clear increasing SOC perturbation by heavy metal atoms can enhance phosphorescence. In a given emission region, $E(T_1)$-$E(S_0)$ is similar and k_p should increase with the decrease of $E(T_1)$-$E(S_1)$, that is ΔE_{ST}. [1–3]

Photophysical measurements:

UV-Vis spectra were recorded on a HITACHI U-3900 spectrophotometer. The steady-state emission spectra and lifetime studies were measured with Edinburgh FL 900 photon-counting

system. Both wavelength-dependent excitation and emission responses of the fluorometer were calibrated. Spectral grade solvents (Merck) were used as received. To determine the photoluminescence quantum yield in solution, samples were degassed using at least three freeze-pump-thaw cycles. The solution quantum yields are calculated using the standard sample which has a known emission quantum yield, according to the following equation

$$\Phi = \Phi_R \frac{I}{I_R}\frac{A_R}{A}\frac{\eta^2}{\eta_R^2} \quad (2)$$

where Φ is the PL quantum yield, the subscript R refers to the reference compound of known quantum yield, I is the integrated fluorescence intensity and η is the refractive index of solvent. A is the absorbance at the excitation wavelength with the measured absorbance between 0.02 ~ 0.05.

Electrochemistry:

Cyclic voltammetry was conducted on a CHI621A Electrochemical Analyzer. Ag/Ag^+ (0.01 M $AgNO_3$) electrode was employed as reference electrode. The oxidation and reduction potentials were measured using platinum working electrode with 0.1 M of NBu_4PF_6 as electrolyte in CH_2Cl_2 and using a gold wire as working electrode with 0.1 M of NBu_4PF_6 in THF, respectively. The potentials were referenced externally to the ferrocenium/ferrocene (Fc^+/Fc) couple.

Photodegradation experiments:

The studied complexes were dissolved in anhydrous toluene with conc. of 5×10^{-5} M, which was transferred to UV cuvettes equipped with Teflon stopcock. These cuvettes were degassed via four freeze-pump-thaw cycles and refilled with argon. All solutions were irradiated with simulated solar irradiation of 620 W m^{-2} using an Atlas Suntest CPS+ Xenon Test Instrument at 35 °C. The irradiation intervals were chosen individually for each sample solution. After each irradiation cycle, the sample solutions were analyzed using Edinburgh fluorometer (FLS920). The emitter concentration was determined from their emission intensity under constant excitation power. The rate constants (k) for the photoinduced decomposition reaction can be obtained using the integrated first-order rate law:

$$\ln\left(\frac{A_t}{A_0}\right) = -kt \quad (3)$$

where t is time in hour, A_t is the emission intensity after t hours degradation and A_0 is the initial emission intensity.

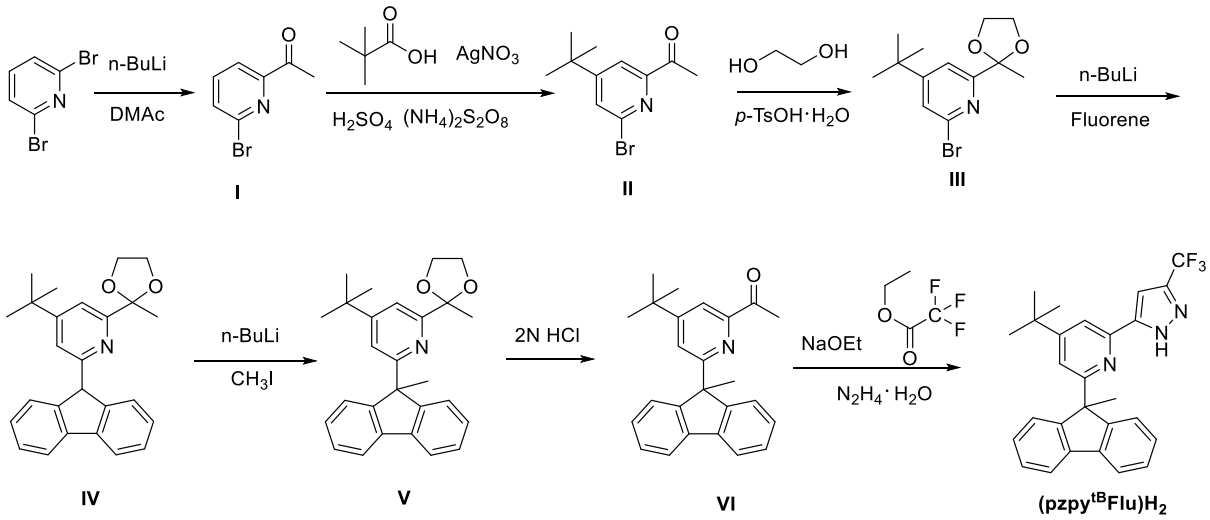
Computational Method:

All calculations were performed with the Gaussian 09 program package.[4] The geometry optimization of ground states of the Ir(III) complexes are simulated with density functional theory (DFT) at the B3LYP/LANL2DZ (Ir) and B3LYP/6-31g(d,p) (H, C, N, F, O) levels using CH_2Cl_2 solvent. The optimized structures of Ir(III) complexes are next employed to calculate the five lowest singlet ($S_0 \rightarrow S_5$) and triplet optical electronic transitions ($S_0 \rightarrow T_5$) using the time–dependent density functional theory (TD-DFT) method. The solvent effect is based on the polarizable continuum model (PCM), which is implemented in the Gaussian program. The electron excitation analysis was completed by using the Multiwfn 3.7 program package.[5]

Synthetic detail:

The dicarbene pincer chelate, i.e. di-hexafluorophosphate salts of 1,3-bis(3-methylimidazolium-1-yl)-5-(trifluoromethyl)benzene [$(mimf)H_3\cdot(PF_6)_2$] and 1,3-bis(3-isopropylimidazolium-1-yl)-5-(trifluoromethyl)benzene [$(pimf)H_3\cdot(PF_6)_2$] were synthesized following the procedures as reported in literature.[6,7]

Synthetic procedures for 4-(tert-butyl)-2-(9-methyl-9H-fluoren-9-yl)-6-(3-(trifluoromethyl)-1H-pyrazol-5-yl)pyridine (**$(pzpy^{tB}Flu)H_2$**)



Scheme S2. Synthetic route of **$(pzpy^{tB}Flu)H_2$.**

To a 250 ml two-neck round-bottom flask, 2,6-dibromopyridine (10 g, 42.2 mmol) was added, and followed by pumping and refilling the flask with N_2 3 times. Anhydrous diethyl ether (120 ml) was injected and the solution was cooled down to -78 °C. 18.6 ml *n*-BuLi (2.5 M in hexane, 46.5 mmol) was dropwise added with stirring. After 1 h, dimethylacetamide (6 ml in 20

ml anhydrous diethyl ether) was added dropwise and, then, allowed the reaction to warm up to RT slowly. The mixture was left in stirring for another 4 h before quenched with 10 ml water. The mixture was extracted into ethyl acetate (EA) and the organic layer was dried with Na_2SO_4. After removal of solvent and purification with silica gel chromatography (EA/hexane, 1/10 in V/V), 1-(6-bromopyridin-2-yl)ethan-1-one (**I**) was obtained as white solid. (yield: 80%, 6.8 g). ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.97 (d, *J* = 7.0 Hz, 1H), 7.76 – 7.59 (m, 2H), 2.69 (d, *J* = 2.3 Hz, 3H).

$AgNO_3$ (0.70 g, 4.1 mmol), **I** (4.1 g, 20.4 mmol) and 150 ml water were added into a 500 ml round-bottom flask immersed in an ice bath. Next, H_2SO_4 (1.7 ml, 32 mmol), pivalic acid (16.2 ml,136 mmol) and $(NH_4)_2S_2O_8$ (32.8g 143.5 mmol) were added with vigorous stirring. The mixture was gently heated to reflux (with obvious evolution of gas) for 8 h. After cooled to RT, the reaction mixture was filtered with Celite, neutralized with saturated Na_2CO_3 solution and washed with water. The solvent was removed under reduced pressure and the residue was purified with column chromatography (EA/hexane, 1/10 in V/V). 1-(6-Bromo-4-(tert-butyl)pyridin-2-yl)ethan-1-one (**II**) was obtained as yellow oil: (yield: 52%, 2.73g). ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.98 (s, 1H), 7.60 (s, 1H), 2.68 (s, 3H), 1.32 (s, 9H).

To a 50 ml round-bottom flask, **II** (2.2 g 8.6 mmol), ethylene glycol (3.1 ml, 85.8 mmol) and *p*-toluenesulfonic acid monohydrate (*p*-TsOH·H_2O, 204.6 mg, 0.9 mmol) were added. The mixture was dissolved with 20 ml toluene and heated to reflux overnight with a Dean-Stark apparatus for removing moisture. After work up, 2-bromo-4-(tert-butyl)-6-(2-methyl-1,3-dioxolan-2-yl)pyridine (**III**) (2.4 g, 93%) was obtained as colorless liquid. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.47 (s, 1H), 7.34 (s, 1H), 4.10 – 4.05 (m, 2H), 3.90 – 3.84 (m, 2H), 1.70 (s, 3H), 1.29 (s, 9H).

Fluorene (2.6 g, 15.6 mmol) was dissolved in anhydrous THF (100 ml), then the solution was cooled to -40 °C and 6.3 ml *n*-BuLi (2.5 M in hexane) was added dropwise. The mixture was allowed to warm up to RT slowly and reacted for another 12 h. After addition of **III** (2.35 g, 7.8 mmol) in 30 ml anhydrous THF at -40 °C, the mixture was stirred at RT for another 12 h. After then, the mixture was quenched by addition of 3 ml water. After removing the solvent, the crude product was washed with brine and purified by column chromatography (EA/hexane, 1/2 in V/V) to give 4-(tert-butyl)-2-(9H-fluoren-9-yl)-6-(2-methyl-1,3-dioxolan-2-yl)pyridine (**IV**) as viscous light yellow oil (1.7 g, 56%). ^{1}H NMR (400 MHz, acetone-d_6) δ 7.90 (d, *J* = 7.6 Hz, 2H), 7.56 (d, *J* = 7.5 Hz, 2H), 7.47 (d, *J* = 1.7 Hz, 1H), 7.41 (t, *J* = 7.4 Hz, 2H), 7.31 (td, *J* = 7.5, 1.2 Hz, 2H), 6.80 (d, *J* = 1.8 Hz, 1H), 5.35 (s, 1H), 4.09 – 4.00 (m, 2H), 3.98 – 3.86 (m, 2H), 1.75 (s, 3H), 1.14 (s, 9H).

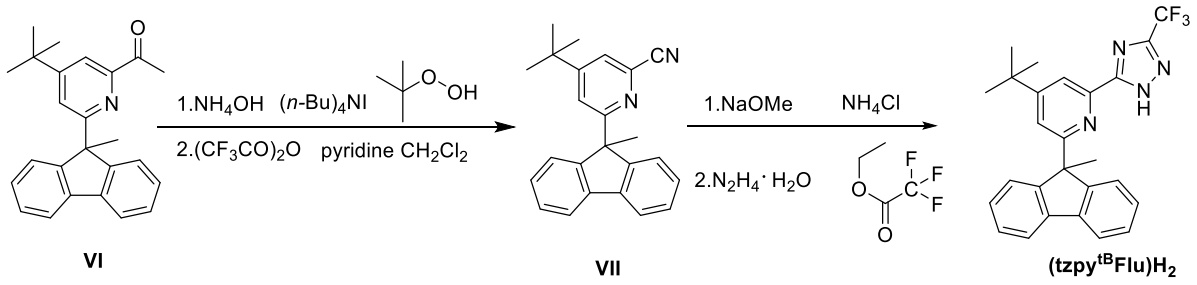
IV (2.7 g, 7 mmol) was dissolved in anhydrous THF (80 ml) and, then, the solution was cooled to -78 °C, to which 3.4 ml *n*-BuLi (2.5 M in hexane) was added dropwise. The reaction mixture was stirred at -20 °C for 1 h. Methyl iodide (0.87 g, 14 mmol) in 5 ml anhydrous THF was added, and the resulting mixture was stirred at RT for another 3 h and, next, was quenched by

addition of 3 ml methanol. After removing the solvent, the residues was washed with brine, and purified by column chromatography (EA/hexane, 1/2 in V/V), giving 4-(tert-butyl)-2-(2-methyl-1,3-dioxolan-2-yl)-6-(9-methyl-9H-fluoren-9-yl)pyridine (**V**) as viscous light yellow oil (1.76 g, 63%). ^{1}H NMR (400 MHz, acetone-d_6) δ 7.86 (d, J = 7.9 Hz, 2H), 7.61 (d, J = 7.4 Hz, 2H), 7.39 (d, J = 7.2 Hz, 2H), 7.36 (d, J = 1.3 Hz, 1H), 7.32 (t, J = 8.0 Hz, 2H), 6.70 (d, J = 1.7 Hz, 1H), 4.11 – 4.06 (m, 2H), 3.98 – 3.93 (m, 2H), 1.95 (s, 3H), 1.81 (s, 3H), 1.06 (s, 9H).

To a 50 ml flask**, V** (1.83 g, 4.6 mmol) in 10 ml 2N HCl were refluxed for 4 h. The reaction mixture was dissolved in EA and washed with aqueous $NaHCO_3$ to yield 1-(4-(tert-butyl)-6-(9-methyl-9H-fluoren-9-yl)pyridin-2-yl)ethan-1-one (**VI**) as white solid (1.57 g, 96%). ^{1}H NMR (400 MHz, acetone-d_6) δ 7.90 (d, J = 7.5 Hz, 2H), 7.82 (d, J = 1.8 Hz, 1H), 7.59 (d, J = 7.5 Hz, 2H), 7.41 (td, J = 7.5, 1.2 Hz, 2H), 7.36 – 7.31 (td, J = 7.5, 1.2 Hz, 2H), 6.97 (d, J = 1.8 Hz, 1H), 2.80 (s, 3H), 2.02 (s, 3H), 1.09 (s, 9H).

Sodium ethoxide (160 mg, 2.3 mmol) in a 50 ml two-neck flask was put into an ice bath under N_2 atmosphere. **VI** (0.71 g, 2 mmol) in 10 ml anhydrous THF was added and stirred for 30 min. Ethyl trifluoroacetate (0.42 g, 2.9 mmol) was injected and the mixture was heated to 70 °C for 12 h. After cooled to RT, water was added and the reaction mixture was concentrated on a rotary evaporator. The residue was dissolved in EA and washed with diluted HCl solution. After removal of EA and drying under vacuum, $N_2H_4 \cdot H_2O$ (0.33 g, 5.9 mmol), p-$TsOH \cdot H_2O$ (37 mg, 0.2 mmol) and 20 ml ethanol (EtOH) was added and refluxed overnight. Removal of EtOH and purification with column chromatography yielded **(pzpy^{tB}Flu)H$_2$** as white solid (0.58 g, 65%). ^{1}H NMR (400 MHz, acetone-d_6) δ 12.91 (s, 1H), 7.90 – 7.87 (m, 2H), 7.85 (d, J = 1.6 Hz, 1H), 7.68 – 7.65 (m, 2H), 7.43 – 7.40 (m, 2H), 7.38 (d, J = 1.2 Hz, 1H), 7.36 – 7.30 (m, 2H), 6.69 (d, J = 1.6 Hz, 1H), 2.04 (s, 3H), 1.10 (s, 6H). ^{19}F NMR (376 MHz, acetone-d_6) δ -62.52.

Synthetic procedures for 4-(*tert*-butyl)-2-(9-methyl-9H-fluoren-9-yl)-6-(3-(trifluoromethyl)-1H-1,2,4-triazol-5-yl)pyridine (**(tzpy^{tB}Flu)H$_2$**)



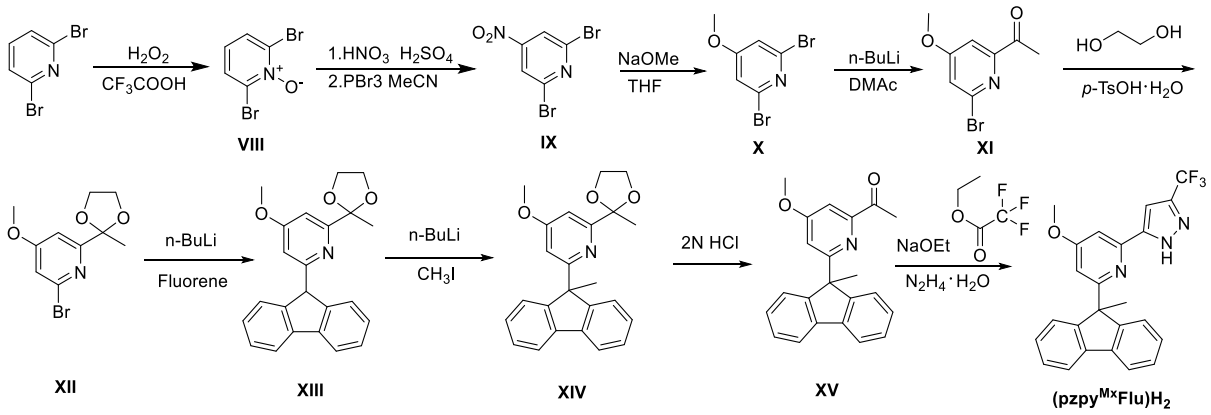
Scheme S3 Synthetic route to dianionic chelate **(tzpy^{tB}Flu)H$_2$**.

VI (2.11 g, 5.93 mmol), NH_3 (aq) (25% in H_2O, 5.57 mL, 88.9 mmol), tetrabutylammonium iodide (1.09 g, 2.96 mmol) and *tert*-butyl hydroperoxide solution (70% in H_2O, 6.0 mL, 47.4 mmol) were charged to a sealed tube and placed in a 100 °C oil bath for 12 h. The reaction mixture was dissolved in EA, washed with brine, and then separated using flash

column chromatography (CH_2Cl_2/methanol, 20/1 in V/V). The amide was obtained as white solid (1.31 g, 62%), which was next dissolved with 20 ml of anhydrous CH_2Cl_2. After adding 3 ml pyridine, the solution was cooled with ice bath and trifluoroacetic anhydride (0.99 mL, 7.09 mmol) was added dropwise. The reaction was stirred for 1 h and quenched with ice water and washed with aqueous $NaHCO_3$. 4-(tert-Butyl)-6-(9-methyl-9H-fluoren-9-yl)picolinonitrile (**VII**, 0.68 g, 41%.) was obtained as yellow liquid after purification with column chromatography (EA/hexane, 1/4 in V/V). ^{1}H NMR (400 MHz, acetone-d_6) δ 7.90 (ddd, J = 7.6, 1.2, 0.7 Hz, 2H), 7.81 (d, J = 1.7 Hz, 1H), 7.49 (ddd, J = 7.5, 1.2, 0.7 Hz, 2H), 7.42 (td, J = 7.5, 1.2 Hz, 2H), 7.34 (td, J = 7.5, 1.2 Hz, 2H), 6.97 (d, J = 1.7 Hz, 1H), 1.94 (s, 3H), 1.10 (s, 9H).

VII (0.68 g, 1.51 mmol) and NaOMe (10 mg, 0.19 mmol) in EtOH (15 mL) was stirred at RT for 12 h. After then, NH_4Cl (97 mg, 1.8 mmol) was added and the resulting mixture was refluxed for 4 h. After cooled to RT, the mixture was concentrated under vacuum. To this mixture was added 2,2,2-trifluoroacetohydrazide (194 mg, 1.5 mmol), NaOH (67 mg, 1.67 mmol) and anhydrous THF (20 mL). After refluxed for 12 hours, the mixture was concentrated and the residue was extracted into ethyl acetate, washed with deionized water three-times and dried over anhydrous Na_2SO_4, and then concentrated to dryness. The crude product was purified by column chromatography, eluting with a mixture of ethyl acetate and hexane (1:7) to afford a white solid **(tzpy^{tB}Flu)H$_2$** (0.31 g, 46%). ^{1}H NMR (400 MHz, acetone-d_6) δ 14.05 (s, 1H), 8.06 (d, J = 1.8 Hz, 1H), 7.94 – 7.90 (m, 2H), 7.67 (dt, J = 7.5, 0.9 Hz, 2H), 7.43 (td, J = 7.5, 1.3 Hz, 2H), 7.35 (td, J = 7.5, 1.2 Hz, 2H), 6.84 (d, J = 1.8 Hz, 1H), 2.07 (s, 3H), 1.14 (s, 9H).

Synthetic procedures for 4-methoxy-2-(9-methyl-9H-fluoren-9-yl)-6-(3-(trifluoromethyl)-1H-pyrazol-5-yl)pyridine (**(pzpy^{Mx}Flu)H$_2$**)



Scheme S4 Synthetic route to dianionic chelate **(pzpy^{Mx}Flu)H$_2$**.

2,6-Dibromopyridine (3 g, 12.7 mmol), 3.6 ml H_2O_2 (35% solution) and 13 ml CF_3CO_2H were added to a 100 ml round-bottom flask. The reaction was kept in 70 °C for 40 h and then pour into ice water after cooling to RT. 2,6-Dibromopyridine 1-oxide (**VIII**) was filtered and washed with ice water 3 times. The crude product was dried under vacuum and used without further

purification (2.8 g, 88%). ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.63 (d, *J* = 8.1 Hz, 2H), 6.91 (t, *J* = 8.1 Hz, 1H).

To a 250 ml round-bottom flask, was added **VIII** (10 g, 39.5 mmol) and 65 ml H_2SO_4, followed by addition of 30 ml mixed solution of H_2SO_4 and HNO_3 (1/1 in V/V) over a period of 25 min. The temperature was gradually raised to 85 °C and kept overnight. After then, the mixture was poured into ice water and with vigorous stirring. The nitration intermediate was collected by filtration and vacuum drying. It was next added into a solution of PBr_3 (3 eq, 11.3 ml, 118.5 mmol) in 50 ml acetonitrile, and refluxed overnight. Acetonitrile and unreacted PBr_3 were removed by reduced pressure distillation, and the residue were neutralized with Na_2CO_3 solution. Purification by flash column chromatography (EA/hexane, 1/10 in V/V) gave 2,6-dibromo-4-nitropyridine (**IX**) as pale-yellow solid (8.5 g, 76% for two steps). ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.17 (d, *J* = 0.5 Hz, 2H).

To a solution of **IX** (5 g, 17.7 mmol) in 100 ml anhydrous THF, sodium methoxide (1.15 g, 21.3 mmol) was added in portions at 0 °C. After stirred at RT for 4 h, 2 ml water was added and THF was removed under reduced pressure. 2,6-Dibromo-4-methoxypyridine (**X**) (4.3 g, 93%) was obtained after column chromatography (EA/hexane, 1/3 in V/V). ^{1}H NMR (400 MHz, chloroform-*d*) δ 6.97 (s, 1H), 3.84 (s, 2H).

Using **X** as starting material and following similar procedure reported for **I** gave 1-(6-bromo-4-methoxypyridin-2-yl)ethan-1-one (**XI**) as white solid (2.5 g, 96%). ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.50 (d, *J* = 2.3 Hz, 1H), 7.14 (d, *J* = 2.3 Hz, 1H), 3.88 (s, 3H), 2.67 (s, 3H).

Using **XI** as starting material and following similar procedure reported for **III** gave 2-bromo-4-methoxy-6-(2-methyl-1,3-dioxolan-2-yl)pyridine (**XII**) as white solid (2.22 g, 93%). ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.03 (d, *J* = 1.9 Hz, 1H), 6.90 (d, *J* = 1.6 Hz, 1H), 4.11 – 4.00 (m, 2H), 3.91 – 3.80 (m, 2H), 3.84 (s, 3H), 1.69 (s, 3H).

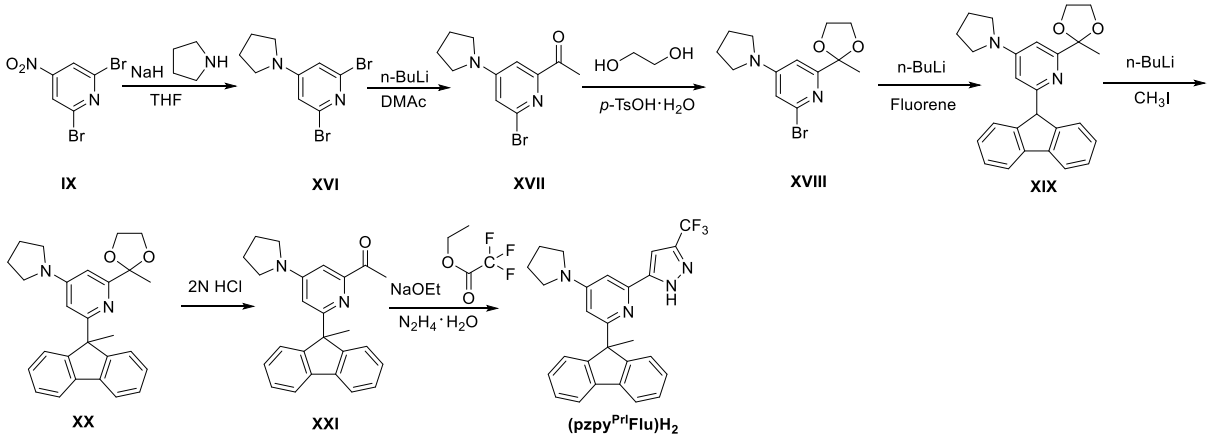
Using **XII** as starting material and following similar procedure reported for **IV** gave 2-(9H-fluoren-9-yl)-4-methoxy-6-(2-methyl-1,3-dioxolan-2-yl)pyridine (**XIII**) as white solid (1.2 g, 51%). ^{1}H NMR (400 MHz, acetone-d_6) δ 7.89 (dt, *J* = 7.6, 0.9 Hz, 2H), 7.55 (dq, *J* = 7.4, 1.0 Hz, 2H), 7.41 (tdd, *J* = 7.5, 1.2, 0.7 Hz, 2H), 7.30 (td, *J* = 7.5, 1.2 Hz, 2H), 6.99 (d, *J* = 2.3 Hz, 1H), 6.19 (d, *J* = 2.3 Hz, 1H), 5.30 (s, 1H), 4.08 – 4.03 (m, 2H), 3.95 – 3.90 (m, 2H), 3.69 (s, 3H), 1.74 (s, 3H).

Using **XIII** as starting material and following similar procedure reported for **V** gave 4-methoxy-2-(2-methyl-1,3-dioxolan-2-yl)-6-(9-methyl-9H-fluoren-9-yl)pyridine (**XIV**) as white solid (1 g, 78%). ^{1}H NMR (400 MHz, acetone-d_6) δ 7.84 (ddd, *J* = 7.5, 1.3, 0.7 Hz, 2H), 7.57 (ddd, *J* = 7.4, 1.3, 0.7 Hz, 2H), 7.37 (td, *J* = 7.4, 1.3 Hz, 2H), 7.30 (td, *J* = 7.4, 1.3 Hz, 2H), 6.92 (d, *J* = 2.2 Hz, 1H), 6.10 (d, *J* = 2.3 Hz, 1H), 4.08 – 4.03 (m, 2H), 3.96 – 3.91 (m, 2H), 3.62 (s, 3H), 1.93 (s, 3H), 1.77 (s, 3H).

Using **XIV** as starting material and following similar procedure reported for **VI** gave 1-(4-methoxy-6-(9-methyl-9H-fluoren-9-yl)pyridin-2-yl)ethan-1-one (**XV**) as white solid (0.92 g, 95%). ^{1}H NMR (400 MHz, acetone-d_6) δ 7.92 – 7.86 (m, 2H), 7.57 (dd, *J* = 7.5, 1.1 Hz, 2H), 7.40 (td, *J* = 7.5, 1.2 Hz, 2H), 7.36 – 7.29 (m, 3H), 6.37 (d, *J* = 2.4 Hz, 1H), 3.72 (s, 3H), 2.78 (s, 3H), 2.01 (s, 3H).

Using **XV** as starting material and following similar procedure reported for **(pzpy^{tB}Flu)H$_2$** gave **(pzpy^{Mx}Flu)H$_2$** as white solid (0.85 g, 73%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.88 (d, *J* = 7.4 Hz, 2H), 7.67 (d, *J* = 7.5 Hz, 2H), 7.48 (d, *J* = 1.6 Hz, 1H), 7.43 (t, *J* = 2.1 Hz, 1H), 7.41 – 7.35 (m, 2H), 7.31 (tdd, *J* = 7.4, 2.4, 1.3 Hz, 2H), 5.98 (t, *J* = 2.1 Hz, 1H), 3.66 (d, *J* = 2.0 Hz, 3H), 2.00 (d, *J* = 1.8 Hz, 3H).

Synthetic procedures for 4-pyrrolidinyl-2-(9-methyl-9H-fluoren-9-yl)-6-(3-(trifluoromethyl)-1H-pyrazol-5-yl)pyridine (**(pzpy^{Prl}Flu)H$_2$**)



Scheme S5 Synthetic route to dianionic chelate **(pzpy^{Prl}Flu)H$_2$**.

To a flask charged with NaH (60% in petrol oil, 0.49 g, 12 mmol), 30 ml anhydrous N,N-dimethylformamide (DMF) was added and cooled to 0 °C. Pyrrolidine (0.83 g, 12 mmol) was added dropwise and stirred for 30 min. **IX** (3 g, 11 mmol) was added and stirred at RT for 3 h. The reaction was quenched by adding 3 ml water. After washing with brine and purification using column chromatography (EA/hexane, 1/1 in V/V), 2,6-dibromo-4-(pyrrolidin-1-yl)pyridine (**XVI**, 2.2 g, 68%) was obtain as colorless oil. ^{1}H NMR (400 MHz, chloroform-*d*) δ 6.48 (d, *J* = 0.9 Hz, 2H), 3.29 – 3.22 (m, 4H), 2.06 – 1.97 (m, 4H).

Using **XVI** as starting material and following similar procedure reported for **I** gave 1-(6-bromo-4-(pyrrolidin-1-yl)pyridin-2-yl)ethan-1-one (**XVII**) as colorless oil (1.4 g, 78%). ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.07 (d, *J* = 2.3 Hz, 1H), 6.62 (d, *J* = 2.3 Hz, 1H), 3.36 – 3.28 (m, 4H), 2.63 (d, *J* = 0.4 Hz, 3H), 2.06 – 2.00 (m, 4H).

Using **XVII** as starting material and following similar procedure as reported for **III** gave 2-bromo-6-(2-methyl-1,3-dioxolan-2-yl)-4-(pyrrolidin-1-yl)pyridine (**XVIII**) as colorless oil (1.5 g, 93%). ^{1}H NMR (400 MHz, acetone-d_6) δ 6.64 (d, *J* = 2.1 Hz, 1H), 6.46 (d, *J* = 2.1 Hz, 1H), 3.99 – 3.93 (m, 2H), 3.85 – 3.81 (m, 2H), 3.36 – 3.27 (m, 4H), 2.04 – 1.97 (m, 4H), 1.55 (s, 3H).

Using **XVIII** as starting material and following similar procedure reported for **VI** gave 2-(9H-fluoren-9-yl)-6-(2-methyl-1,3-dioxolan-2-yl)-4-(pyrrolidin-1-yl)pyridine (**XIX**) as light yellow viscous oil (1.3 g, 55%). ^{1}H NMR (400 MHz, acetone-d_6) δ 7.86 (dt, *J* = 7.6, 1.0 Hz, 2H), 7.57 (dq, *J* = 7.5, 1.0 Hz, 2H), 7.37 (tdd, *J* = 7.5, 1.2, 0.7 Hz, 2H), 7.27 (td, *J* = 7.5, 1.2 Hz, 1H), 6.55 (d, *J* = 2.3 Hz, 1H), 5.72 (d, *J* = 2.3 Hz, 1H), 5.18 (s, 1H), 4.04 – 3.96 (m, 2H), 3.95 – 3.84 (m, 2H), 3.05 (d, *J* = 7.4 Hz, 4H), 1.91 – 1.84 (m, 4H), 1.71 (s, 3H).

Using **XIX** as starting material and following similar procedure reported for **V** gave 2-(2-methyl-1,3-dioxolan-2-yl)-6-(9-methyl-9H-fluoren-9-yl)-4-(pyrrolidin-1-yl)pyridine (**XX**) as light yellow viscous oil (1.2 g, 78%). ^{1}H NMR (400 MHz, acetone-d_6) δ 7.81 (ddd, *J* = 7.5, 1.3, 0.7 Hz, 2H), 7.62 (ddd, *J* = 7.4, 1.3, 0.7 Hz, 2H), 7.34 (td, *J* = 7.4, 1.3 Hz, 2H), 7.28 (td, *J* = 7.4, 1.3 Hz, 2H), 6.49 (d, *J* = 2.2 Hz, 1H), 5.69 (d, *J* = 2.2 Hz, 1H), 4.05 – 3.97 (m, 2H), 3.96 – 3.88 (m, 2H), 3.01 – 2.96 (m, 4H), 1.90 (s, 3H), 1.86 – 1.81 (m, 4H), 1.76 (s, 3H).

Using **XX** as starting material and following similar procedure reported for **VI** gave 1-(6-(9-methyl-9H-fluoren-9-yl)-4-(pyrrolidin-1-yl)pyridin-2-yl)ethan-1-one (**XXI**) as colorless solid (1.1 g, 97%).^{1}H NMR (400 MHz, chloroform-*d*) δ 7.75 (ddd, *J* = 7.5, 1.2, 0.7 Hz, 2H), 7.54 (ddd, *J* = 7.5, 1.2, 0.7 Hz, 2H), 7.35 (td, *J* = 7.4, 1.2 Hz, 2H), 7.27 (td, *J* = 7.4, 1.2 Hz, 2H), 6.96 (d, *J* = 2.3 Hz, 1H), 5.85 (d, *J* = 2.3 Hz, 1H), 3.04 (s, 4H), 2.84 (s, 3H), 1.98 (s, 3H), 1.86 – 1.81 (m, 4H).

Using **XXI** as starting material and following similar procedure reported for **(pzpy^{tB}Flu)H$_2$** gave **(pzpy^{Prl}Flu)H$_2$** as colorless solid (0.8 g, 67%). ^{1}H NMR (400 MHz, acetone-d_6) δ 12.77 (s, 1H), 7.87 (d, *J* = 7.5 Hz, 2H), 7.72 (d, *J* = 7.5 Hz, 2H), 7.44 – 7.36 (m, 2H), 7.35 – 7.30 (m, 2H), 7.28 (s, 1H), 6.94 (d, *J* = 2.1 Hz, 1H), 5.76 (d, *J* = 2.1 Hz, 1H), 3.08 (s, 4H), 2.03 (s, 3H), 1.92-1.87 (m, 4H).

Synthetic procedures for Iridium (III) complexes studied in this work.

Ir(III) metal complexes **Flu-1**–**5** were obtained in 15 ~ 37% of yields using similar procedures as reported in refference.[8,9]

Synthetic and spectral data of **Flu-1**: Yield: 26%. ^{1}H NMR (600 MHz, Acetone-d_6) δ 8.24 (dd, *J* = 20.2, 2.0 Hz, 2H), 8.14 (d, *J* = 2.0 Hz, 1H), 8.03 (d, *J* = 2.0 Hz, 1H), 8.02 (d, *J* = 7.5 Hz, 1H), 7.78 (t, *J* = 8.8 Hz, 3H), 7.50 (td, *J* = 7.5, 1.3 Hz, 1H), 7.44 (td, *J* = 7.4, 1.1 Hz, 1H), 7.28 (d, *J* = 2.1 Hz, 1H), 7.13 (s, 1H), 7.06 (dd, *J* = 7.2, 1.1 Hz, 1H), 6.85 (d, *J* = 2.1 Hz, 1H), 6.39 (t, *J* = 7.5 Hz, 1H), 5.81 (dd, *J* = 7.6, 1.1 Hz, 1H), 3.50 (s, 3H), 2.37 (s, 3H), 1.89 (s, 3H), 1.48 (s, 9H).

^{19}F NMR (565 MHz, acetone-d_6) δ -59.99 (s, 3 F), -60.28 (s, 3 F).FD MS: m/z 943.3 $(M)^+$. Anal. Calcd. for $C_{42}H_{34}F_6IrN_7$: C, 53.50; H, 3.63; N, 10.40. Found: C, 53.38; H, 3.61; N, 10.26.

Single crystal of **Flu-1** was obtained by slowly mixing its saturated dichloromethane solution with methyl alcohol. Selected crystal data of **Flu-1**: $C_{43}H_{38}F_6IrN_7O$; M = 975.00; triclinic; space group = P-1 (no. 2); a = 12.6904(3) Å, b = 13.1740(3) Å, c = 13.7421(3) Å; α = 112.8180(10)°, β = 99.5400(10)°, γ = 108.3300(10)°; V = 1898.43(8) Å^3; Z = 2; F(000) = 968.0, crystal size = 0.39 × 0.17 × 0.03 mm^3; λ(Mo-Kα) = 0.71073 Å; T = 173(2) K; μ = 3.592 mm^{-1}; 40907 reflections collected, 13213 independent reflections (R_{int} = 0.0339, R_{sigma} = 0.0373), data / restraints / parameters = 13213 / 0 / 540, GOF = 1.026, final $R_1[I > 2\sigma(I)]$ = 0.0213 and wR_2(all data) = 0.0483. Data available at https://www.ccdc.cam.ac.uk (deposition number: 2030785).

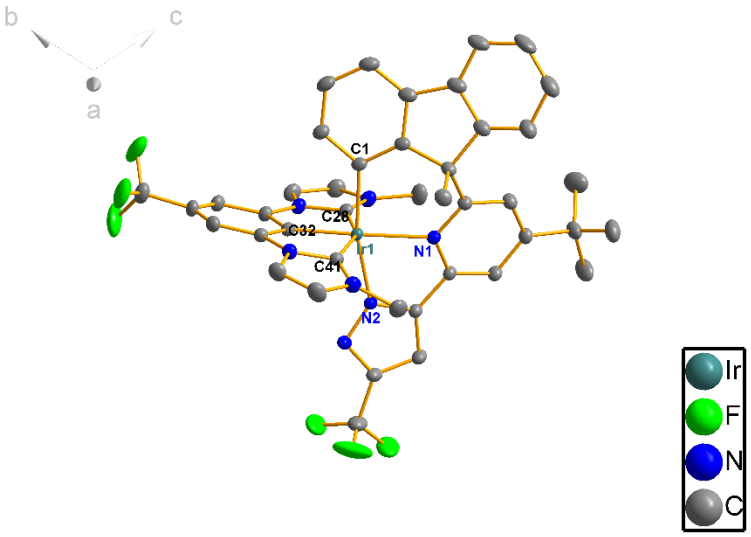


Fig. **S1** Crystal structure of **Flu-1** with thermal ellipsoids shown at the 50% probability level. Hydrogen atoms and solvate molecules were omitted for clarity. Selected bond lengths (Å) and angles (°): Ir1-C32 = 1.9545(17); Ir1-C41= 2.0478(17); Ir1-C1 = 2.0702(16); Ir1-C28 = 2.0712(16); Ir1-N2 = 2.1014(14); Ir1-N1 = 2.1813(15); C32-Ir1-C41 = 77.21(7); C32-Ir1-C28 = 77.96(7); C41-Ir1-C28 = 154.96(7); C1-Ir1-N2 = 167.19(6); C1-Ir1-N1 = 91.34(6); N2-Ir1-N1 = 76.06(5).

Synthetic and spectral data of **Flu-2**: Yield: 31%. ^{1}H NMR (400 MHz, acetone-d_6) δ 8.23 (dd, J = 9.2, 2.1 Hz, 2H), 8.13 (d, J = 2.0 Hz, 1H), 8.09 (dd, J = 2.2, 0.6 Hz, 1H), 8.00 (d, J = 7.5 Hz, 1H), 7.78 – 7.73 (m, 3H), 7.51 – 7.46 (m, 1H), 7.45 – 7.38 (m, 2H), 7.11 (d, J = 0.6 Hz, 1H), 7.06 (d, J = 2.2 Hz, 1H), 7.04 (dd, J = 7.3, 1.1 Hz, 1H), 6.40 – 6.34 (m, 1H), 5.82 (dd, J = 7.6, 1.1 Hz, 1H), 4.52 – 4.42 (m, 1H), 2.33 (t, J = 6.7 Hz, 1H), 1.85 (s, 3H), 1.50 (s, 9H), 1.38 (d, J = 6.8 Hz, 3H), 0.72 (d, J = 6.8 Hz, 3H), 0.46 (d, J = 6.5 Hz, 3H), 0.22 (d, J = 6.7 Hz, 3H). ^{19}F NMR (565 MHz, acetone-d_6) δ -60.09 (s, 3 F), -60.33 (s, 3 F). FD MS: m/z 999.3 $(M)^+$. Anal. Calcd. for $C_{46}H_{42}F_6IrN_7$: C, 55.30; H, 4.24; N, 9.81. Found: C, 55.27; H, 4.30; N, 9.77.

Synthetic and spectral data of **Flu-3**: Yield: 37%. ^{1}H NMR (400 MHz, acetone-d_6) δ 8.43 (d, *J* = 2.1 Hz, 1H), 8.28 (d, *J* = 2.2 Hz, 1H), 8.25 (d, *J* = 2.0 Hz, 1H), 8.10 (dd, *J* = 2.3, 0.6 Hz, 1H), 8.03 (d, *J* = 7.5 Hz, 1H), 7.79 (dd, *J* = 1.3, 0.7 Hz, 1H), 7.79 – 7.76 (m, 2H), 7.50 (td, *J* = 7.5, 1.3 Hz, 1H), 7.46 (d, *J* = 2.2 Hz, 1H), 7.43 (td, *J* = 7.4, 1.1 Hz, 1H), 7.09 – 7.04 (m, 2H), 6.39 (t, *J* = 7.5 Hz, 1H), 5.83 (dd, *J* = 7.6, 1.1 Hz, 1H), 4.38 (p, *J* = 6.7 Hz, 1H), 2.21 (p, *J* = 6.8 Hz, 1H), 1.84 (s, 3H), 1.51 (s, 9H), 1.36 (d, *J* = 6.8 Hz, 3H), 0.66 (d, *J* = 6.9 Hz, 3H), 0.43 (d, *J* = 6.6 Hz, 3H), 0.20 (d, *J* = 6.7 Hz, 3H). ^{19}F NMR (376 MHz, acetone-d_6) δ -60.51 (s, 3 F), -63.77 (s, 3 F). FD MS: m/z 1000.3 $(M)^+$. Anal. Calcd. for $C_{45}H_{41}F_6IrN_8$: C, 54.08; H, 4.13; N, 11.20. Found: C, 54.15; H, 4.08; N, 11.33.

Synthetic and spectral data of **Flu-4**: Yield: 21%. ^{1}H NMR (400 MHz, acetone-d_6) δ 8.21 (dd, *J* = 2.3, 0.5 Hz, 1H), 8.06 (dd, *J* = 2.2, 0.5 Hz, 1H), 7.96 (d, *J* = 7.4 Hz, 1H), 7.75 – 7.70 (m, 4H), 7.68 (d, *J* = 2.6 Hz, 1H), 7.44 (td, *J* = 7.4, 1.5 Hz, 1H), 7.42 – 7.36 (m, 2H), 7.05 (d, *J* = 2.2 Hz, 1H), 7.04 (d, *J* = 0.7 Hz, 1H), 7.02 (dd, *J* = 7.3, 1.1 Hz, 1H), 6.35 (t, *J* = 7.5 Hz, 1H), 5.82 (dd, *J* = 7.6, 1.1 Hz, 1H), 4.51 (p, *J* = 6.7 Hz, 1H), 4.10 (s, 3H), 2.54 (p, *J* = 6.8 Hz, 1H), 1.85 (s, 3H), 1.39 (d, *J* = 6.8 Hz, 3H), 0.74 (d, *J* = 6.9 Hz, 3H), 0.45 (d, *J* = 6.6 Hz, 3H), 0.22 (d, *J* = 6.8 Hz, 3H). ^{19}F NMR (376 MHz, acetone-d_6) δ -60.16 (s, 3 F), -60.35 (s, 3 F). FD MS: m/z 973.2 $(M)^+$. Anal. Calcd. for $C_{43}H_{36}F_6IrN_7O$: C, 53.08; H, 3.73; N, 10.08. Found: C, 53.01; H, 3.68; N, 10.13.

Synthetic and spectral data of **Flu-5**: Yield: 15%. ^{1}H NMR (600 MHz, Acetone-d_6) δ 8.22 (d, *J* = 2.2 Hz, 1H), 8.07 (d, *J* = 2.1 Hz, 1H), 8.02 (d, *J* = 7.5 Hz, 1H), 7.73 (t, *J* = 9.2 Hz, 3H), 7.44 (td, *J* = 7.4, 1.3 Hz, 1H), 7.42 (d, *J* = 2.2 Hz, 1H), 7.41 – 7.38 (m, 1H), 7.35 (d, *J* = 2.5 Hz, 1H), 7.19 (d, *J* = 2.5 Hz, 1H), 7.06 (d, *J* = 2.2 Hz, 1H), 7.02 (dd, *J* = 7.3, 1.1 Hz, 1H), 6.93 (s, 1H), 6.34 (t, *J* = 7.4 Hz, 1H), 5.81 (dd, *J* = 7.6, 1.1 Hz, 1H), 4.70 (p, *J* = 6.7 Hz, 1H), 3.57 (d, *J* = 54.4 Hz, 4H), 2.78 – 2.73 (m, 1H), 2.15 (s, 4H), 1.86 (s, 3H), 1.43 (d, *J* = 6.8 Hz, 3H), 0.77 (d, *J* = 6.8 Hz, 3H), 0.48 (d, *J* = 6.5 Hz, 3H), 0.24 (d, *J* = 6.7 Hz, 3H). ^{19}F NMR (565 MHz, Acetone-d_6) δ -59.94 (s, 3 F), -60.23 (s, 3 F). FD MS: m/z 1012.4 $(M)^+$. Anal. Calcd. for $C_{46}H_{41}F_6IrN_8$: C, 54.59; H, 4.08; N, 11.07. Found: C, 54.71; H, 4.09; N, 11.15.

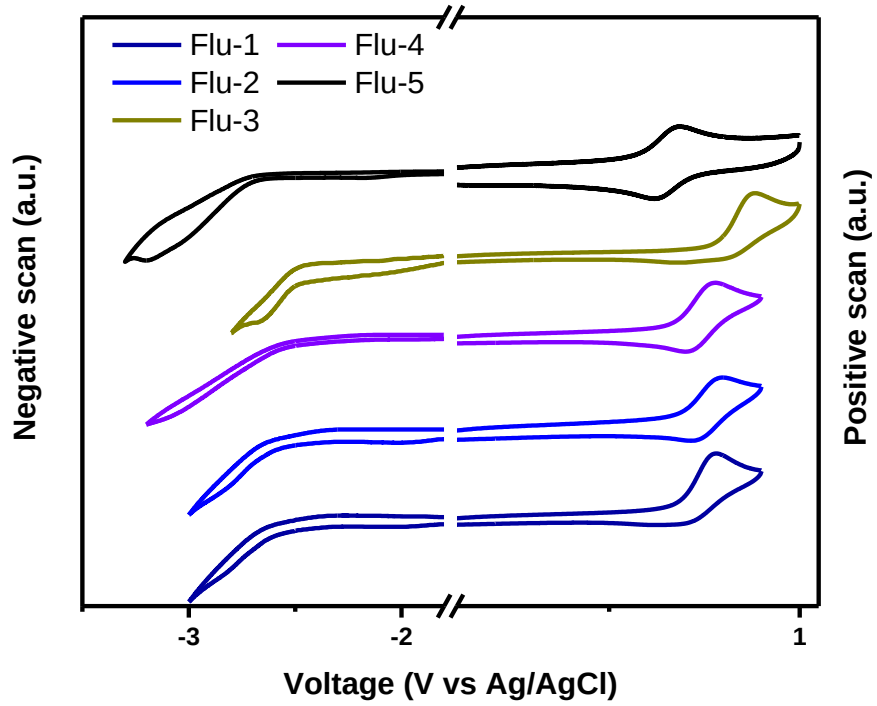


Fig. S2 Cyclic voltammetry study of Ir(III) complexes **Flu-1**–**5**.

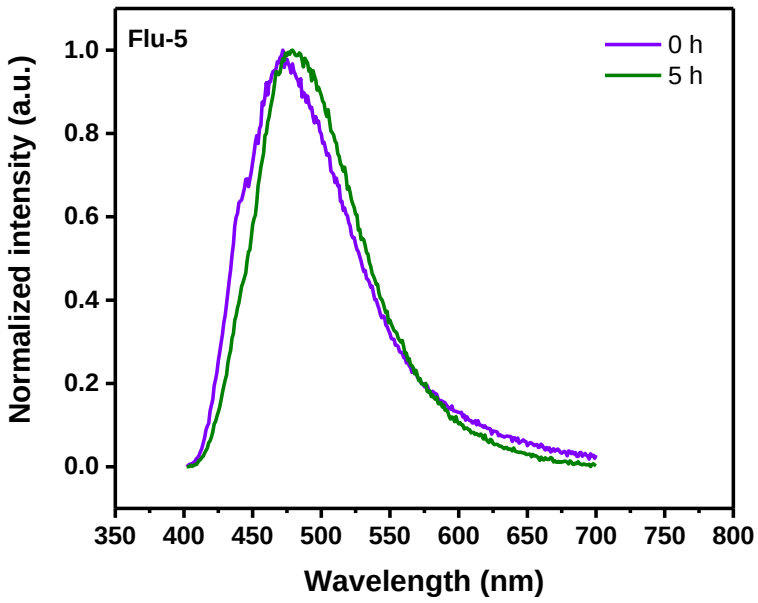


Fig. S3 Emission spectra of **Flu-5** obtained during photodegradation study.

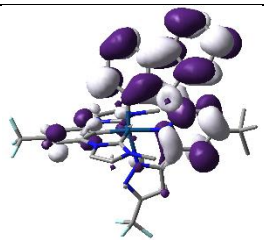
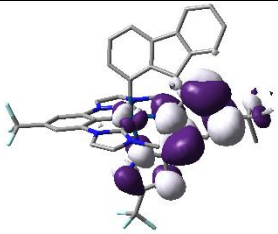
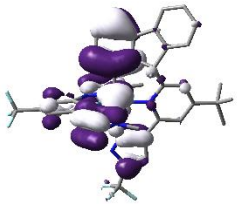
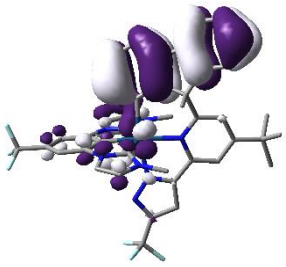
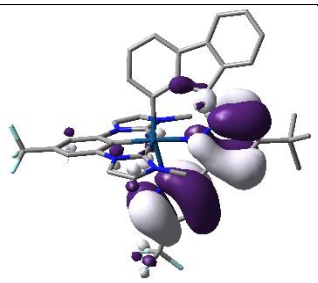
		
LUMO+1	LUMO	HOMO
		
HOMO-2	HOMO-4	

Fig. S4(a). Visualized frontier molecular orbitals of **Flu-1** involved in S_0-T_1 transition.

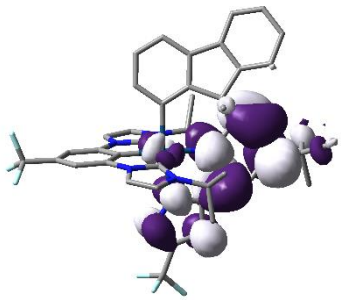
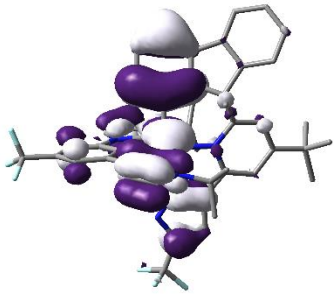
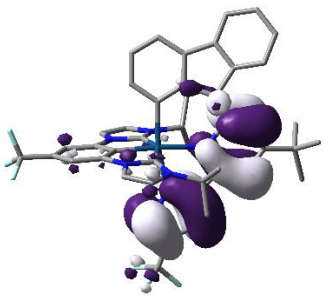
		
LUMO	HOMO	HOMO-4

Fig. S4(b). Visualized frontier molecular orbitals of **Flu-2** involved in S_0-T_1 transition.

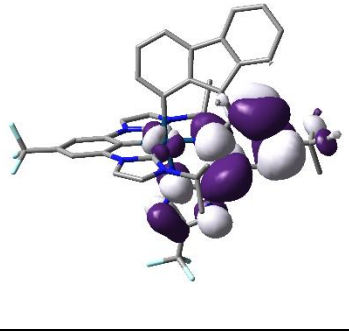
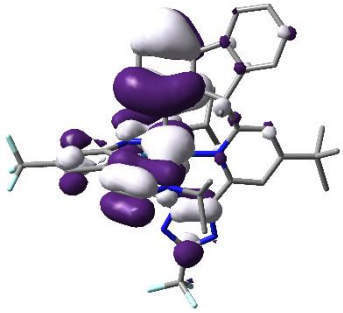
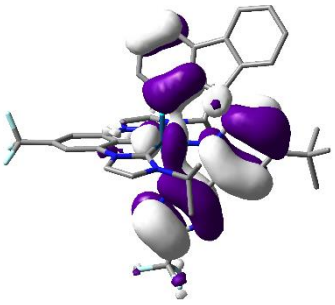
		
LUMO	HOMO	HOMO-5

Fig. S4(c). Visualized frontier molecular orbitals of **Flu-3** involved in S_0-T_1 transition.

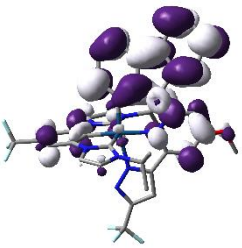
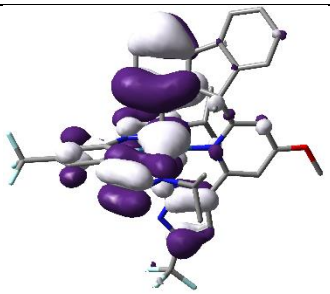
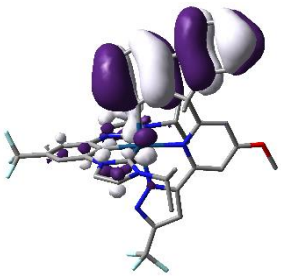
		
LUMO+1	HOMO	HOMO-2

Fig. S4(d). Visualized frontier molecular orbitals of **Flu-4** involved in S_0-T_1 transition.

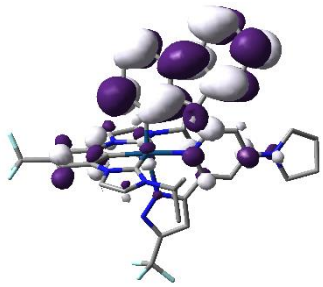
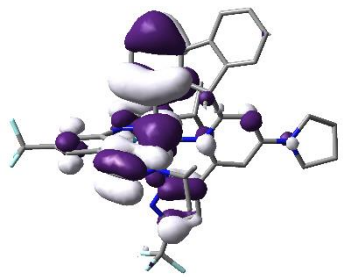
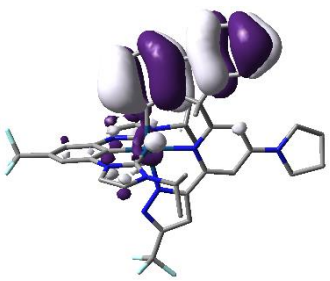
		
LUMO+1	HOMO	HOMO-3

Fig. S4(e). Visualized frontier molecular orbitals of **Flu-5** involved in S_0-T_1 transition.

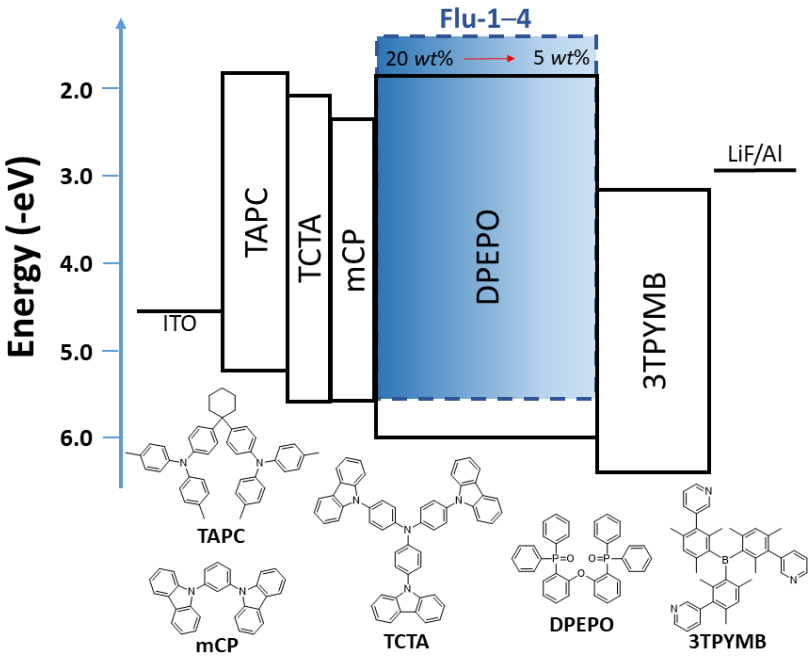


Fig. S5. Device configuration and chemical structures of materials used. ITO/TAPC(20 nm)/TCTA (10 nm)/mCP (10 nm)/ DPEPO: 20-5 wt% dopant (30 nm)/3TPYMB (50 nm)/LiF (1 nm)/Al (120 nm), doping concentration of EML (emissive layer) is linearly decreasing from 20 wt% at the mCP/EML interface to 5 wt% at the EML/3TPYMB interface (shown by gradually fading the color and arrow in EML).

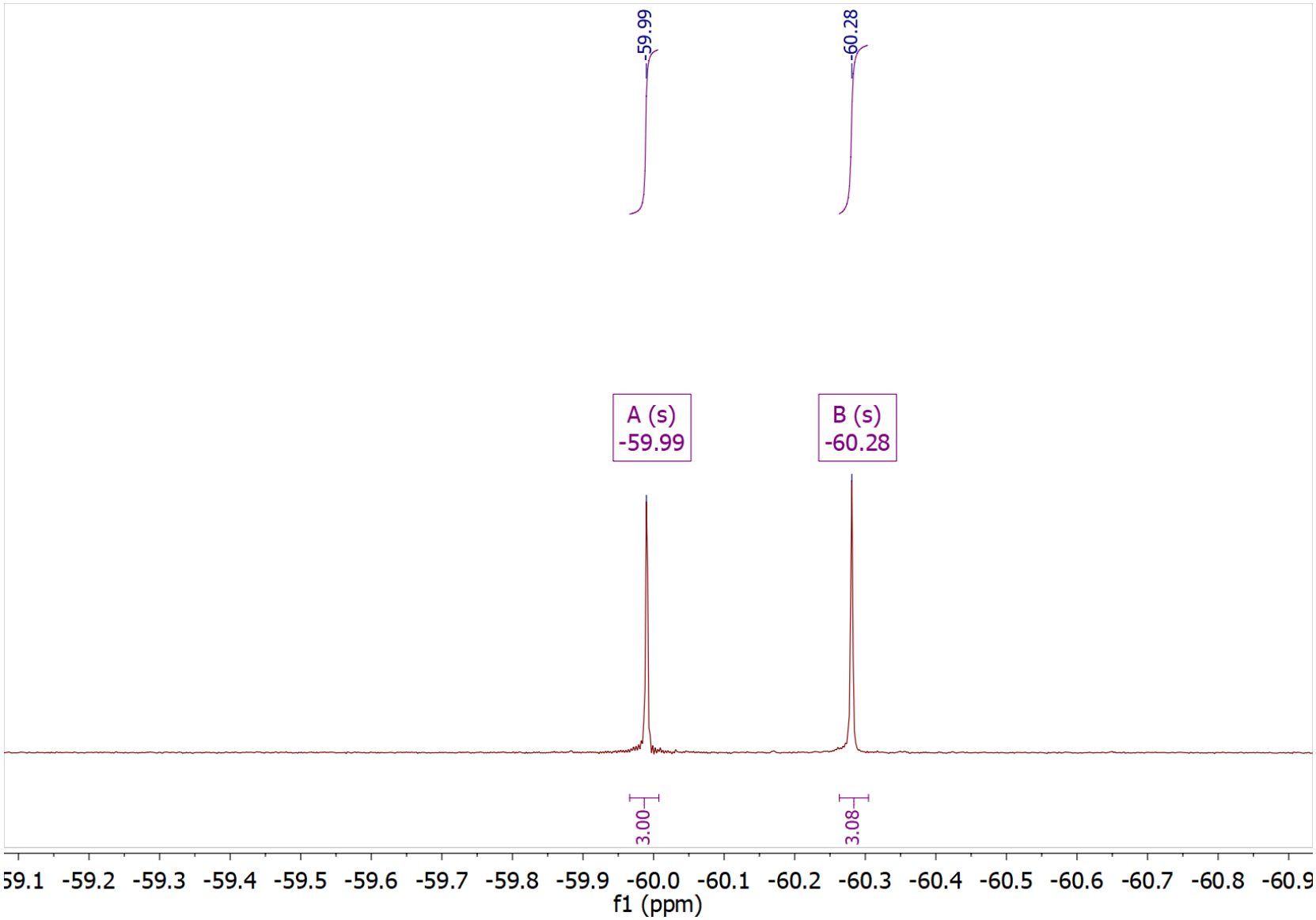


Fig. S6. ^{19}F-NMR spectrum of **Flu-1**.

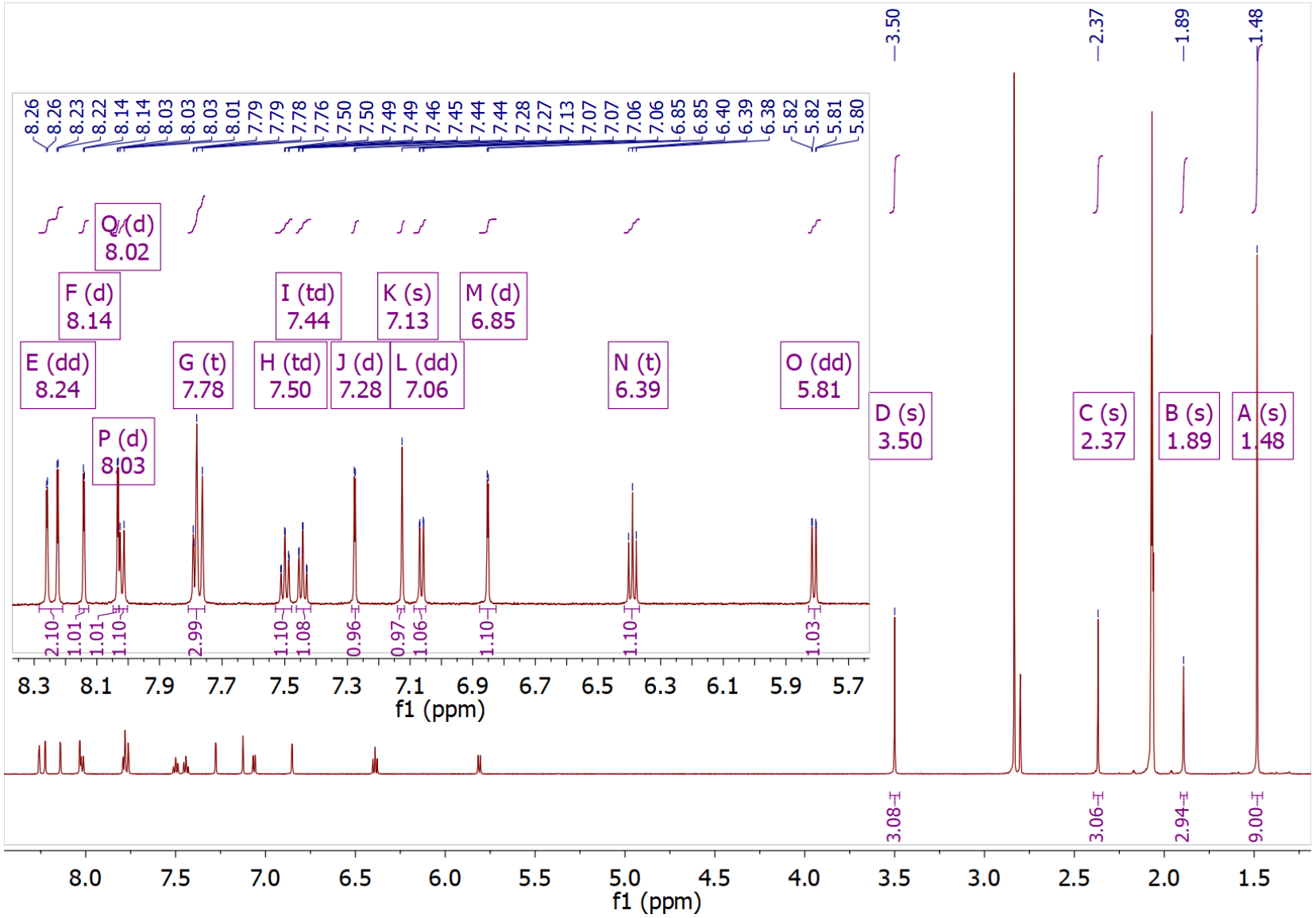


Fig. S7. ^{1}H-NMR spectrum of **Flu-1**.

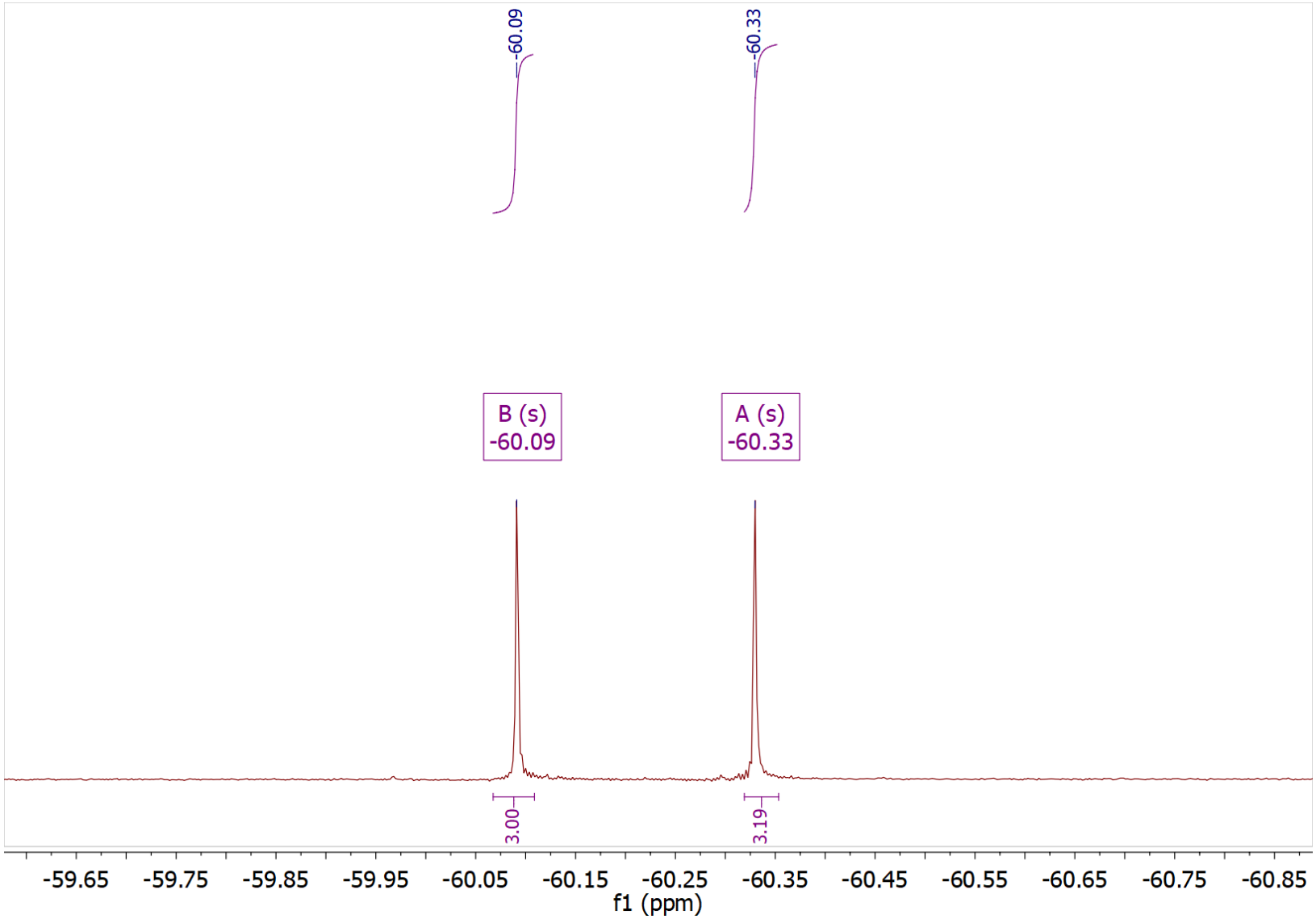


Fig. S8. ^{19}F-NMR spectrum of **Flu-2**.

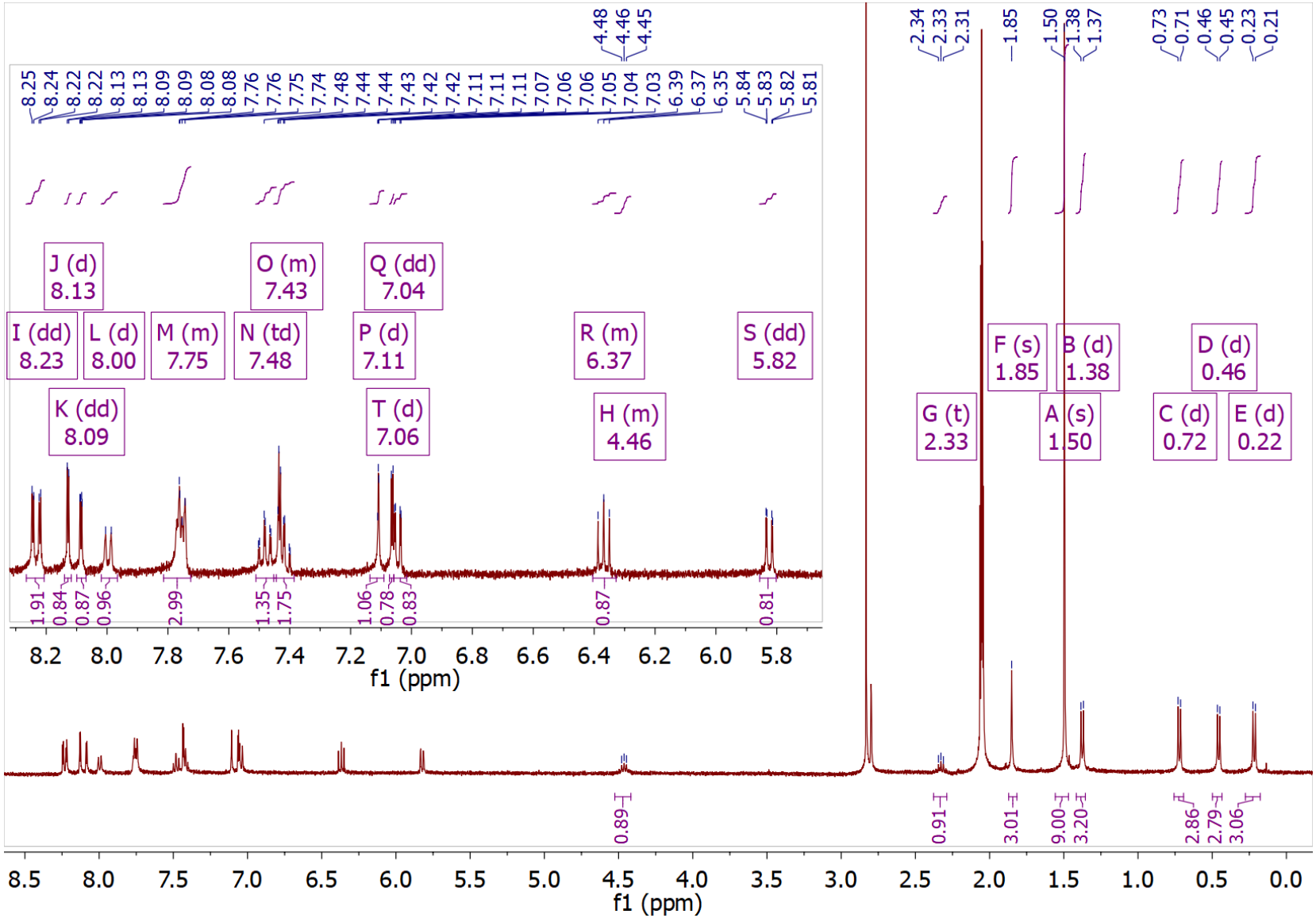


Fig. S9. ^{1}H-NMR spectrum of **Flu-2**.

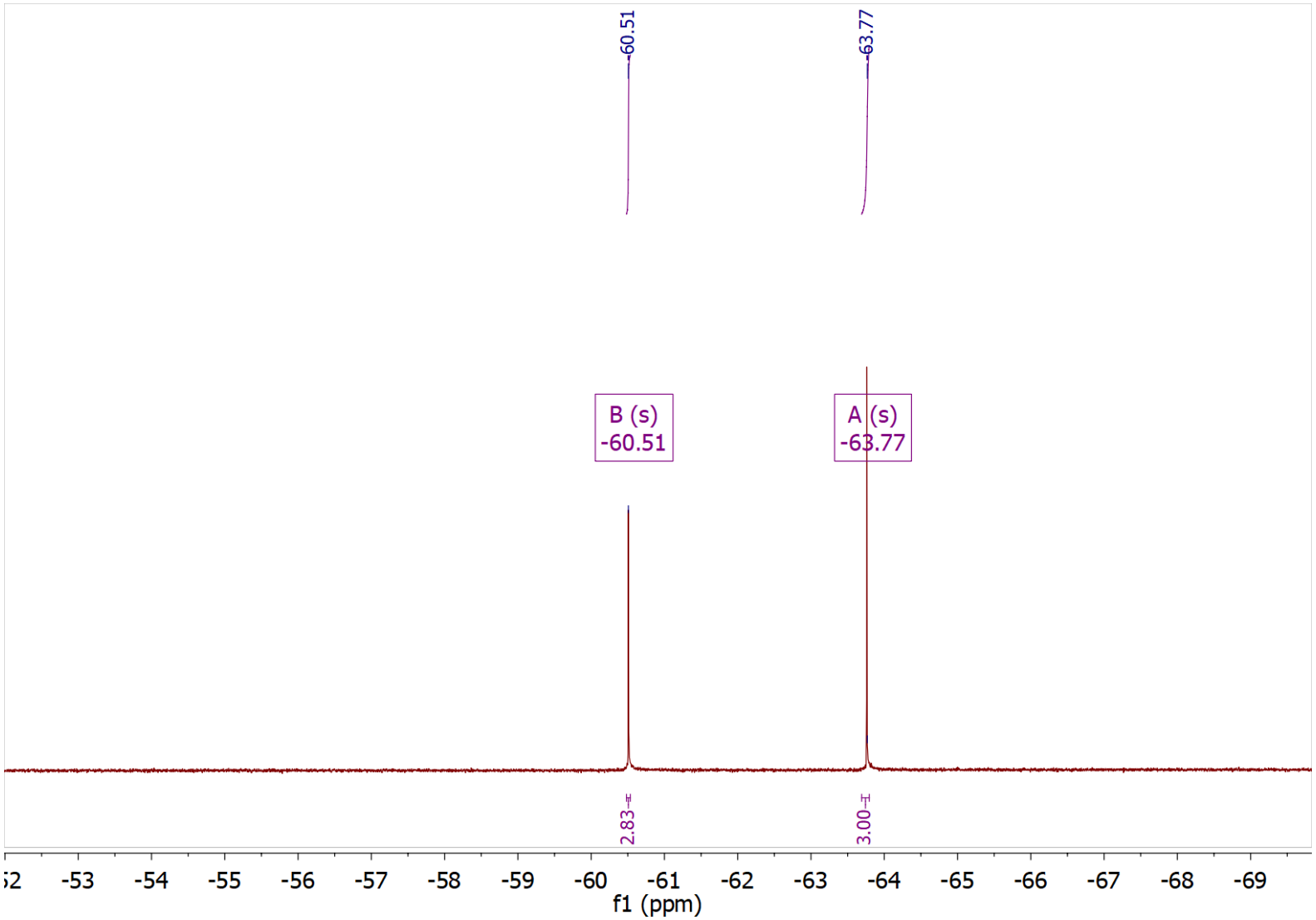


Fig. S10. ^{19}F-NMR spectrum of **Flu-3**.

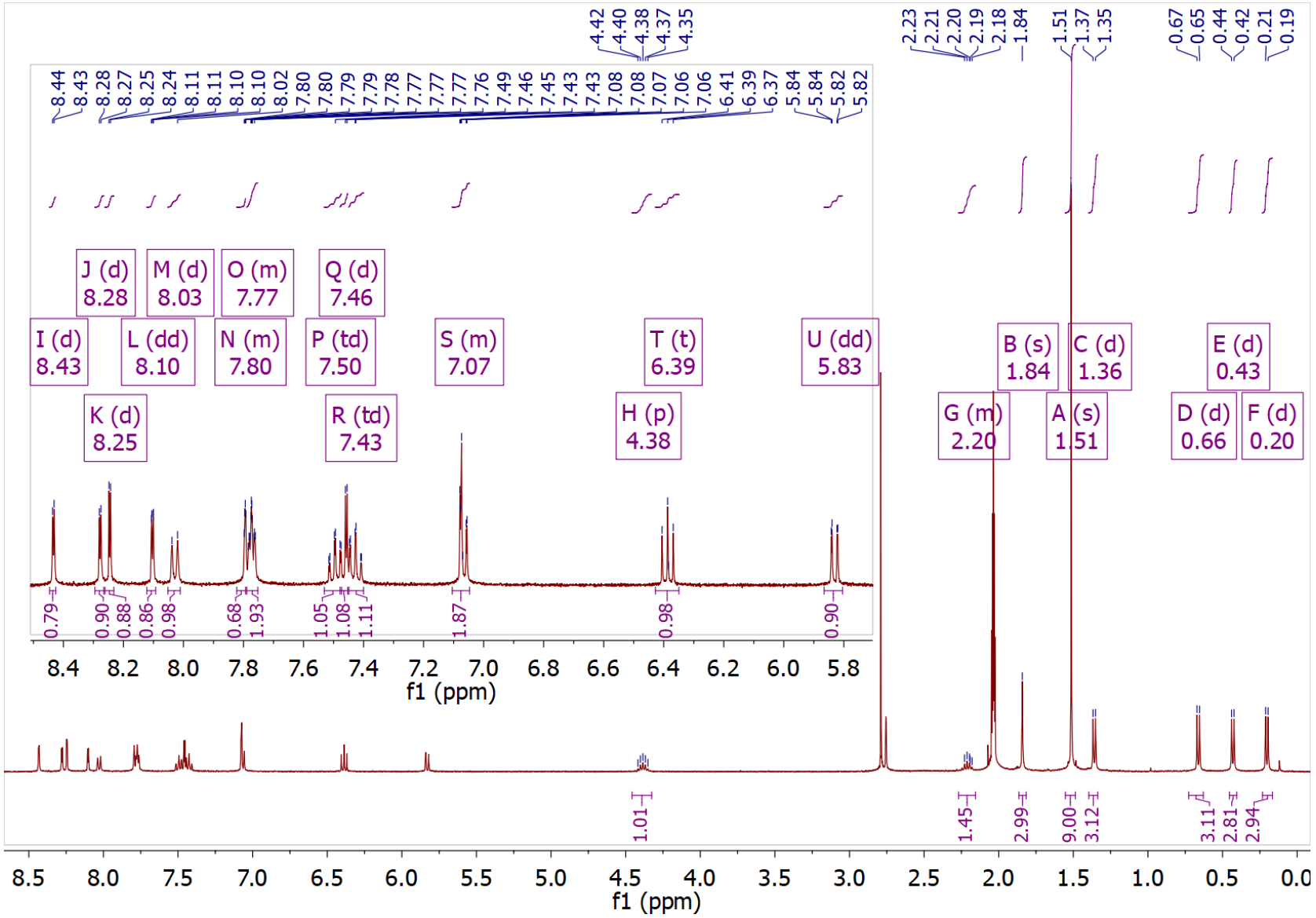


Fig. S11. [1]H-NMR spectrum of **Flu-3**.

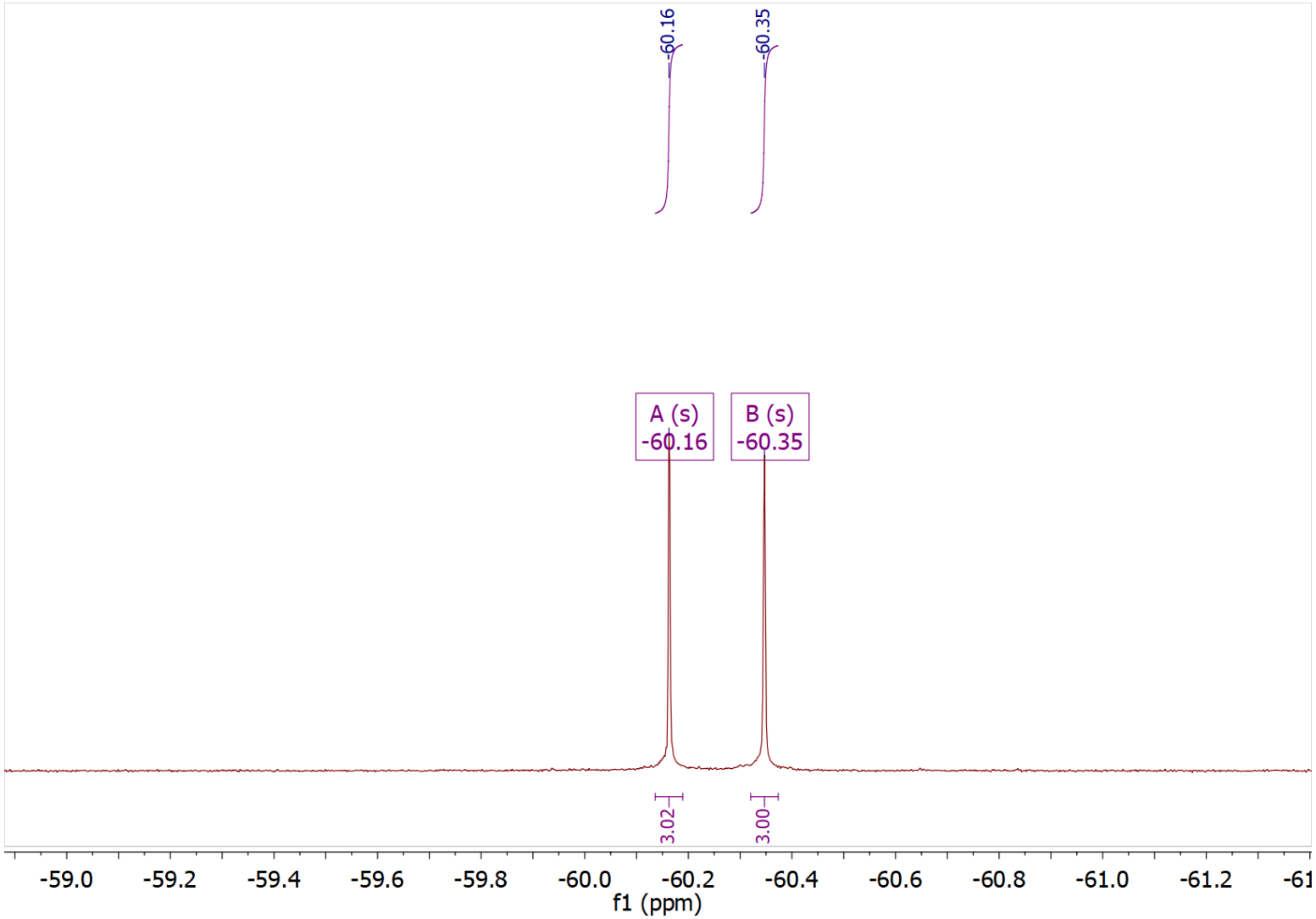


Fig. S12. ^{19}F-NMR spectrum of **Flu-4**.

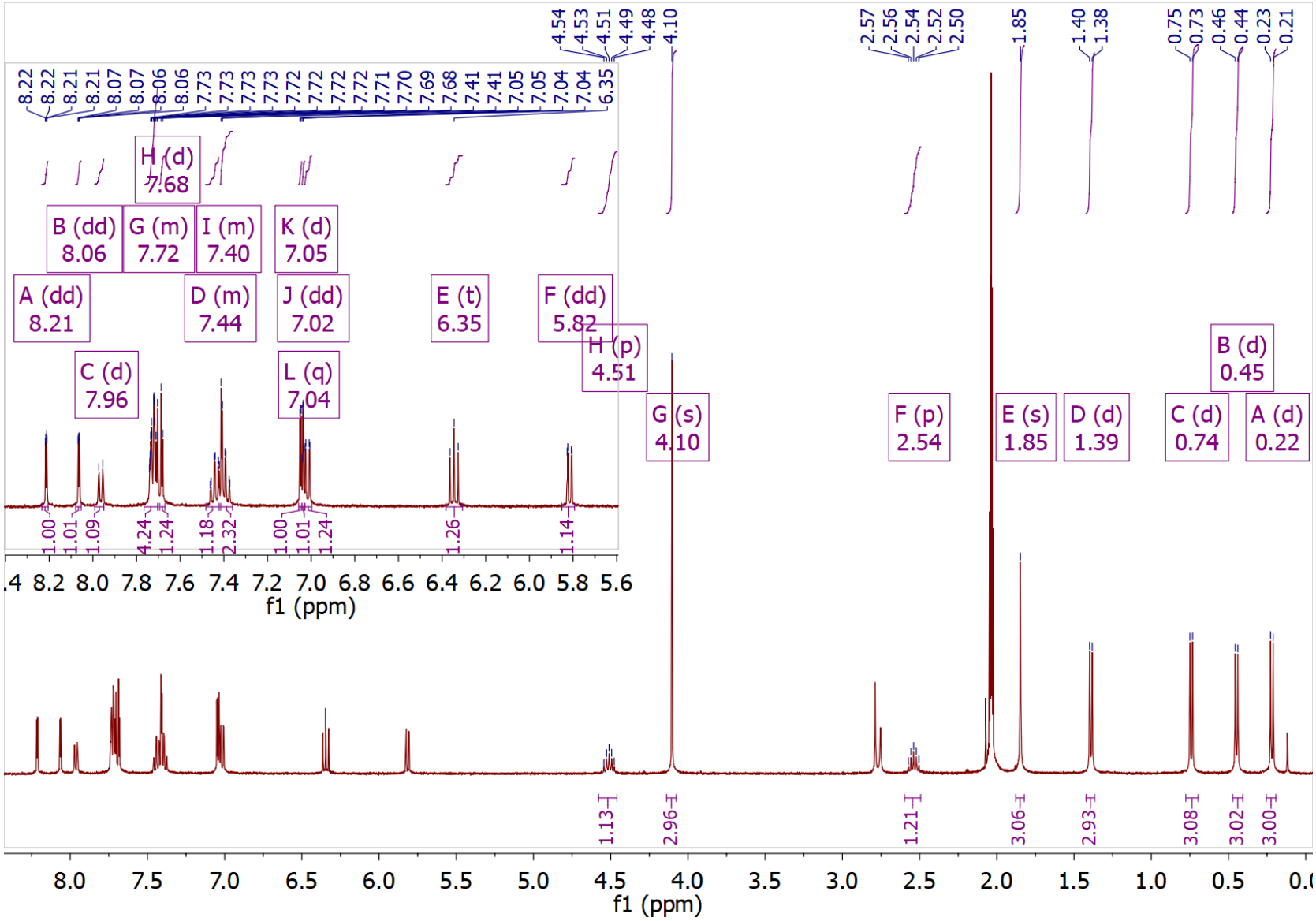


Fig. S13. [1]H-NMR spectrum of **Flu-4**.

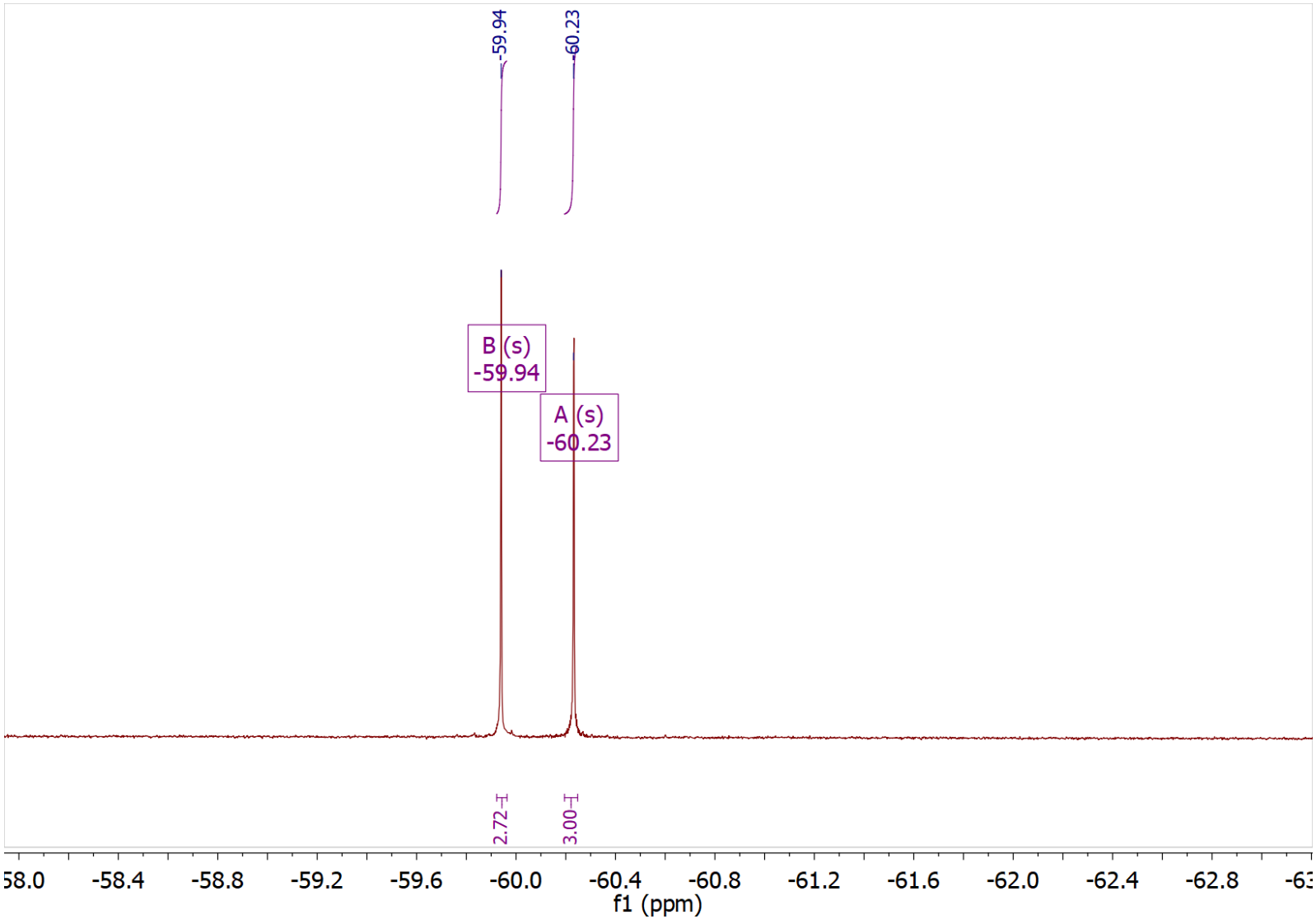


Fig. S14. ^{19}F-NMR spectrum of **Flu-5**.

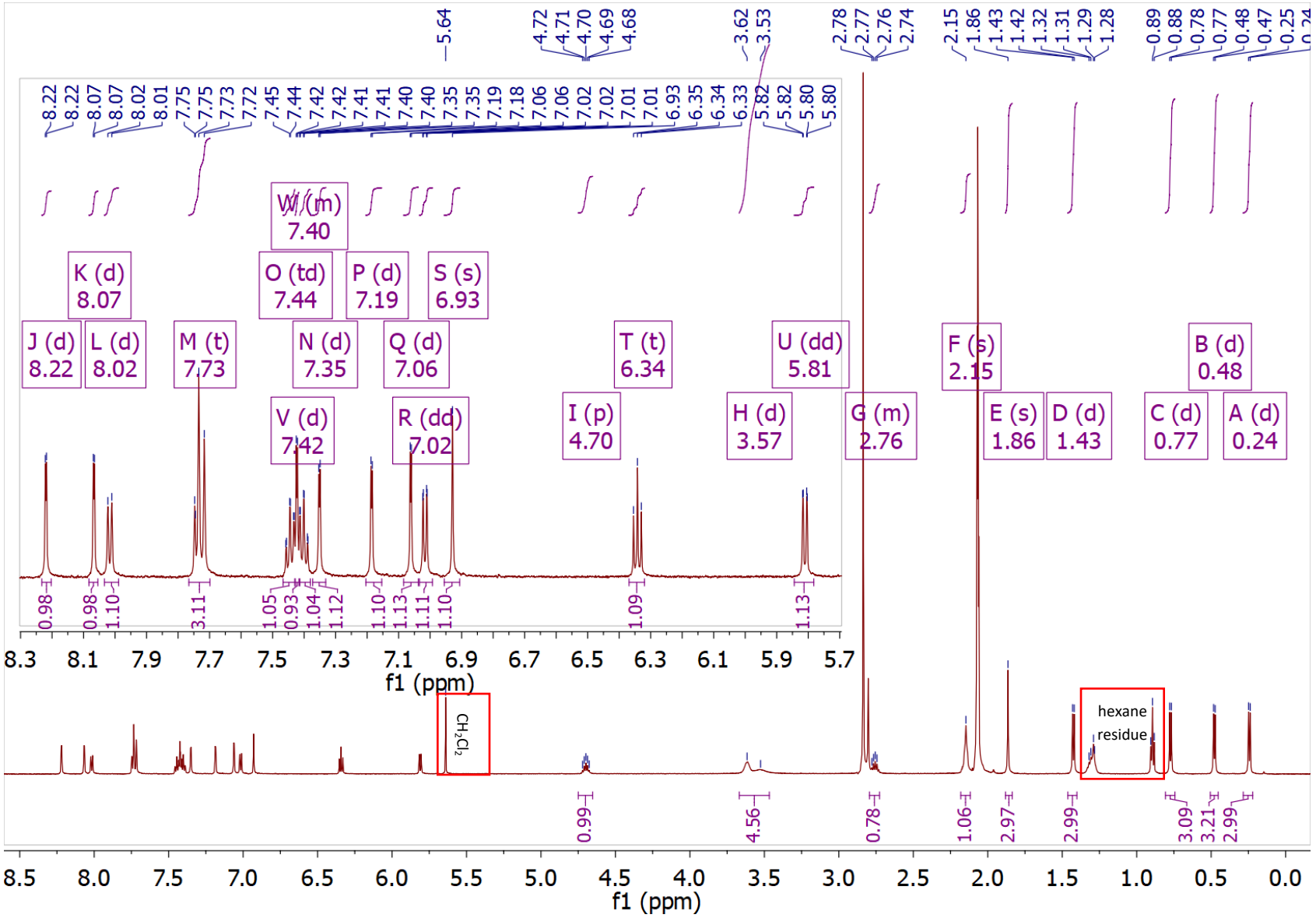


Fig. S15. ^{1}H-NMR spectrum of **Flu-5**.

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