

Supporting Information

Highly efficient circularly polarized phosphorescent electroluminescence from iridium(III) complexes with chiral ligands

Xiao-Yu Zhang,^{a†} Zi-Qi Chen,^{†b} Dong Li,^{†c} Bi-Hai Tong,^{*a,d} Man-Keung Fung,^{*b} Yi-Xiang Cheng^{*c}
and Kong Hui^{*a}

^a School of Metallurgy Engineering, Anhui University of Technology, Maanshan, 243002, Anhui, China. E-mail:
konghui@ahut.edu.cn.

^b Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices, Institute of Functional Nano & Soft
Materials (FUNSOM) & Collaborative Innovation Center of Suzhou Nano Science and Technology, Soochow
University, Suzhou 215123, P. R. China. E-mail: mkfung@suda.edu.cn.

^c Key Lab of Mesoscopic Chemistry of MOE and Jiangsu Key Laboratory of Advanced Organic Materials, School of
Chemistry and Chemical Engineering, Nanjing University, Nanjing 210023, China. E-mail: yxcheng@nju.edu.cn

^d State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing, 210023, China.

[†] These authors contributed equally to this work.

* Corresponding authors.

Contents:

1. General descriptions
2. Intermediate preparation
3. Supplementary data on photophysical properties
4. ¹H- and ¹⁹F-NMR spectra of all new compounds
5. High resolution mass spectrometers (HRMS) of all new compounds
6. References

1. General descriptions

1.1. Materials and characterization

All the materials and solvents were obtained commercially and used as received without further purification. Proton NMR spectra were measured on a Bruker AV400 spectrometer. High resolution mass spectra (HRMS) were recorded with an Agilent Technologies 6530 Accurate-Mass Q-TOF mass spectrometer. X-ray crystallography diffraction was carried out on a Bruker SMART Apex CCD diffractometer. Thermogravimetric analysis (TGA) was recorded on FBS-WTGA instrument. Cyclic voltammetry (CV) was measured on a CHI1140B Electrochemical Analyzer through a three-electrode system with a glassy carbon disk as the working electrode, platinum plate as the counter electrode and Ag/AgCl as the reference electrode. UV-Vis absorption spectra were recorded on a Purkinje General TU-1901 spectrophotometer. The PL spectra were recorded on a PerkinElmer LS-55 fluorescence spectrophotometer. The PL quantum efficiency and lifetime were measured with an Edinburgh FLS980 instrument. The circular dichroism (CD) spectra were measured on a Jasco J-810 circular dichroism spectrometer with 'Low' sensitivity. The scan speed was set as 200 nm/min with 1 nm resolution and a respond time of 1.0 s. The circularly polarized photoluminescence (CPPL) spectra were measured on a Jasco CPL-300 spectrophotometer with 'Standard' sensitivity at 200 nm/min scan speed and respond time of 2.0 s employing "slit" mode.

1.2. Computational methodology

B3LYP functional was used to optimize the geometrical structures of ground state (S_0).^[1] A "double- ξ " quality basis set consisting of Hay and Wadt's effective core potentials (ECP), LANL2DZ,^[2] was employed to the Ir atom. 6-31G(d) basis set^[3] was applied to other nonmetallic atoms. The solvent effect in CH_2Cl_2 medium was considered throughout the calculations. Combined with VMD program,^[5] the molecular orbital was visualized by Multiwfn code.^[4] The frontier molecular orbital (FMO) distribution in molecules was analyzed by Multiwfn using Mulliken population analysis. Gaussian 16 software package was used for calculations.^[6]

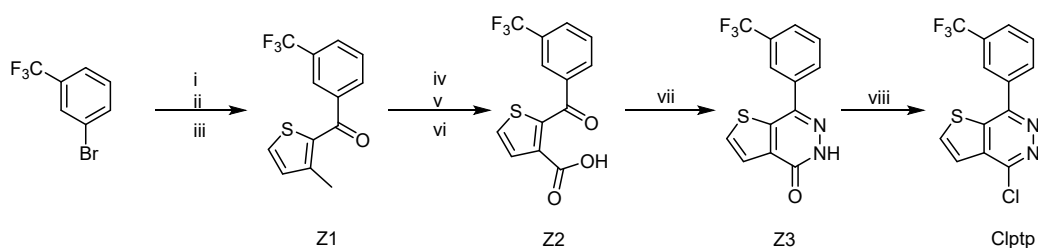
1.3. OLED fabrication

The OLEDs were grown on pre-patterned ITO coated glass ($\approx 20 \Omega \text{ square}^{-1}$). Before depositing into the evaporation system, the ITO substrates were cleaned with acetone, ethyl alcohol,

and deionized water by ultrasonic cleaning machine for 20 min. All the devices were deposited sequentially under fine vacuum of 8×10^{-5} Pa. The organic transport materials were grown by the rate of 0.08-0.15 nm s⁻¹, while organic dopants, LiQ were deposited at the rate of 0.02-0.15 Å s⁻¹, Al was deposited by the rate of 3 Å s⁻¹. The CIE coordinates, luminance, and EL spectra were carried out by a PR655 spectra-scan photometer simultaneously. The current density-voltage characteristics were tested by a programmable Keithley source-measure 2400 and PR655 spectra-scan.

ITO and Aluminum were used as the anode and cathode, respectively. 1, 4, 5, 8, 9, 11-Hexaazatriphenylene-hexacarbonitrile (HAT-CN) and 8-hydroxyquinolinolato-lithium (LiQ) were used as the hole-injection and electron-injection materials, respectively. Di-[4-(N, N-ditolyl-amino)-phenyl] cyclohexane (TAPC) was used as the hole-transport material and N, N, N-tris(4-(9-carbazolyl)phenyl)amine (TCTA) was used as the hole-transport/electron-blocking material. 1,3-Bis(9H-carbazol-9-yl)benzene (mCP) was served as the host material. 1, 3, 5-Tri [(3-pyridyl)-phen-3-yl]benzene (TmPyPB) was used as the electron-transport/hole-blocking material.

2. Intermediate preparation



Scheme S1 Synthetic routes of intermediates: i) Mg, THF, 40 °C, 1 h; ii) 3-Methylthiophene-2-formaldehyde, THF, r. t., 2 h; iii) Dess-Martin periodinane, CH₂Cl₂, r. t., 12 h; iv) NBS, dibenzoyl peroxide, CCl₄, reflux, 12 h; v) AgNO₃, ethanol/H₂O, reflux, 1 h; vi) Jones reagent, acetone, 0 °C, 2 h; vii) Hydrazine hydrate, ethanol, reflux, 12 h; viii) POCl₃, CHCl₃, reflux, 12 h.

(3-Methylthiophen-2-yl)(3-(trifluoromethyl)phenyl)methanone (Z1): To a solution of Grignard reagents (40 mmol) prepared from 3-bromotrifluoromethylbenzene and magnesium in dry THF (40 mL), the solution of 3-methylthiophene-2-formaldehyde (2.52 g, 20 mmol) in dry THF (20 mL) was added at room temperature (r. t.), and the resulting mixture was stirred at this temperature for 2 h. The reaction was quenched by the addition of sat. NH₄Cl (10 mL). The mixture was extracted with EtOAc (3 × 40 mL). The combined organic extracts were dried with Na₂SO₄ and concentrated in vacuo. The alcohol intermediate crude product was dissolved in CH₂Cl₂ (30 mL) and Dess-Martin periodinane (12.72 g, 30 mmol) was added, then the mixture was stirred at r. t. for 12 h. The

reaction was quenched by the addition of aq. NaOH (0.1 mol/L) and was extracted with EtOAc (3 × 40 mL). The combined organic extracts were dried with Na₂SO₄ and concentrated in vacuo. Flash column chromatography using petroleum ether/ethyl acetate (V:V=8:1) as the eluent afforded Z1 (light yellow liquid, 52%). ¹H NMR (400 MHz, CDCl₃) δ 8.08 (s, 1H), 8.00 (d, *J* = 7.8 Hz, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.61 (t, *J* = 7.8 Hz, 1H), 7.54 (d, *J* = 4.9 Hz, 1H), 7.04 (d, *J* = 4.9 Hz, 1H), 2.51 (s, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ -62.56 (s, 3F). HRMS ((+)-ESI): *m/z* = 271.0401 (calcd. 271.0404 for [C₁₃H₁₀F₃OS] [M+H]⁺).

2-(3-(Trifluoromethyl)benzoyl)thiophene-3-carboxylic acid (Z2): A solution of Z1 (0.27 g, 1 mmol), NBS (0.53g, 3 mmol) and dibenzoyl peroxide (0.048 g, 0.2 mmol) in CCl₄ (30 mL) was reflux for 12 h under nitrogen. The precipitate was filtered and washed with dichloromethane, and the resulting solution was washed with sat. NaHCO₃. The combined organic extracts were dried with Na₂SO₄ and concentrated in vacuo. The dibromomethyl intermediate crude product was dissolved in ethanol (30 mL)/H₂O (3 mL) and AgNO₃ (0.51 g, 3 mmol) was added, then the mixture was reflux for 1 h. The precipitate was filtered and washed with ethanol. The resulting solution is evaporated to near dryness, and 50 mL H₂O was added, then extracted with EtOAc (3 × 40 mL). The combined organic extracts were dried with Na₂SO₄ and concentrated in vacuo. The aldehyde ketone intermediate crude product was dissolved in acetone (30 mL) and Jones reagent (2 mL, 2 M) was added in an ice water bath and the mixture was stirred at this temperature for 2 h. The reaction was quenched by the addition of methanol and was extracted with EtOAc (3 × 40 mL). The combined organic extracts were dried with Na₂SO₄ and concentrated in vacuo. Flash column chromatography using CH₂Cl₂/methanol (V:V=20:1) as the eluent afforded Z2 (white solid, 56%). ¹H NMR (400 MHz, CDCl₃) δ 8.10 (s, 1H), 8.00 (d, *J* = 7.8 Hz, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.77 (d, *J* = 5.1 Hz, 1H), 7.66 (d, *J* = 5.2 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 1H). ¹⁹F NMR (376 MHz, CDCl₃) δ -62.88 (s, 3F). HRMS ((+)-ESI): *m/z* = 301.0150 (calcd. 301.0146 for [C₁₃H₈F₃O₃S] [M+H]⁺).

7-(3-(Trifluoromethyl)phenyl)thieno[2,3-*d*]pyridazin-4(5*H*)-one (Z3): A solution of Z2 (0.30 g, 1 mmol) and NH₂NH₂·H₂O (0.50 g, 10 mmol) in ethanol (15 mL) was reflux for 12 h under nitrogen. The precipitate of product S3 was filtered and washed with ethanol, then dried in an oven (yellow solid, 82%). ¹H NMR (400 MHz, DMSO-*d*₆) δ 13.20 (s, 1H), 8.18 (d, *J* = 5.2 Hz, 2H), 8.14 (s, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.84 (t, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 5.2 Hz, 1H). ¹⁹F NMR (376 MHz,

CDCl_3) δ -61.31 (s, 3F). HRMS ((+)-ESI): m/z = 297.0303 (calcd. 297.0309 for $[\text{C}_{13}\text{H}_8\text{F}_3\text{N}_2\text{OS}]$ $[\text{M}+\text{H}]^+$).

4-Chloro-7-(3-(trifluoromethyl)phenyl)thieno[2,3-*d*]pyridazine (Clptp): A solution of Z3 (0.59 g, 2 mmol) and POCl_3 (3.06 g, 20 mmol) in CHCl_3 (20 mL) was reflux for 12 h under nitrogen. The reaction was quenched by the addition of aqueous ammonia and was extracted with CH_2Cl_2 (3×40 mL). The combined organic extracts were dried with Na_2SO_4 and concentrated in vacuo. Flash column chromatography using CH_2Cl_2 as the eluent afforded ZCl (white solid, 91%). ^1H NMR (400 MHz, CDCl_3) δ 8.39 (s, 1H), 8.30 (d, $J = 7.7$ Hz, 1H), 8.01 (d, $J = 5.4$ Hz, 1H), 7.84 (d, $J = 7.7$ Hz, 1H), 7.74 (t, $J = 7.6$ Hz, 1H), 7.72 (d, $J = 5.2$ Hz, 1H). ^{19}F NMR (376 MHz, CDCl_3) δ -62.72 (s, 3F).

3. Supplementary data on photophysical properties

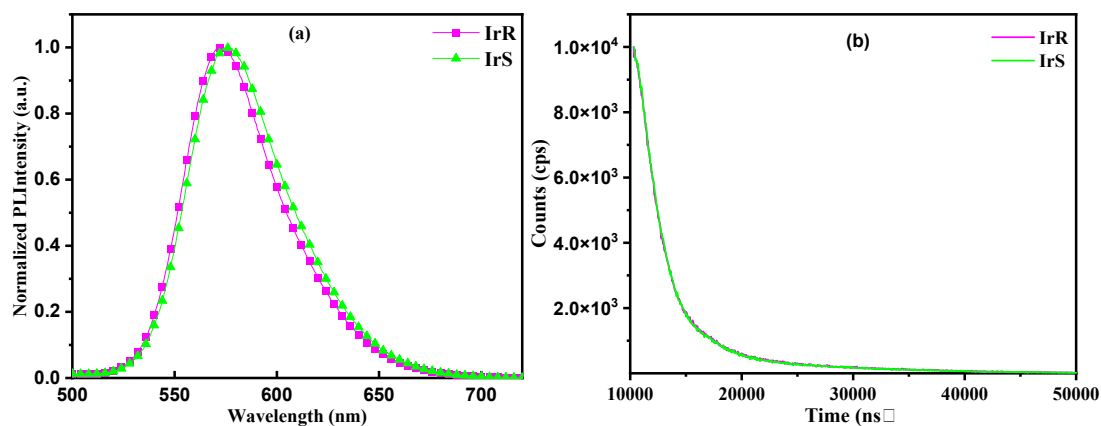
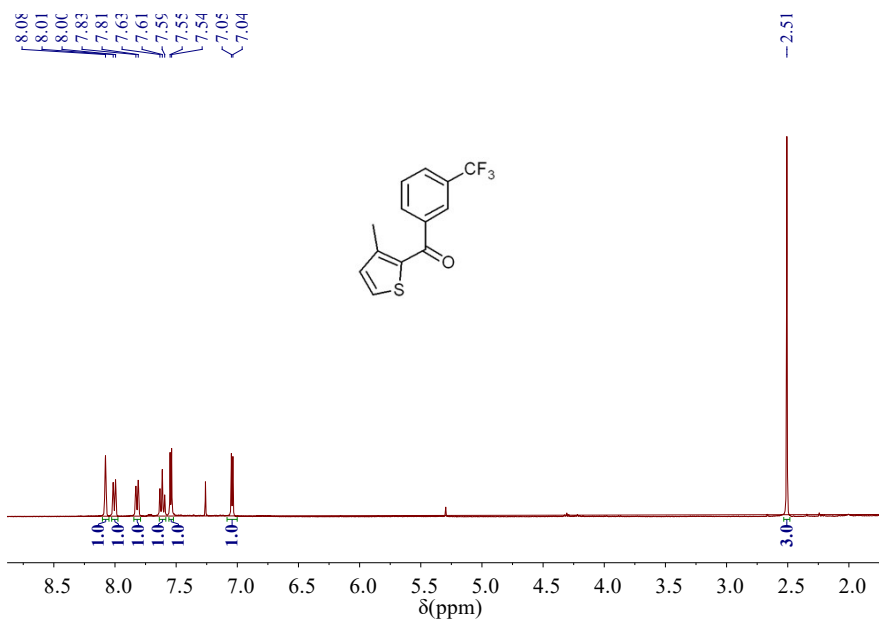


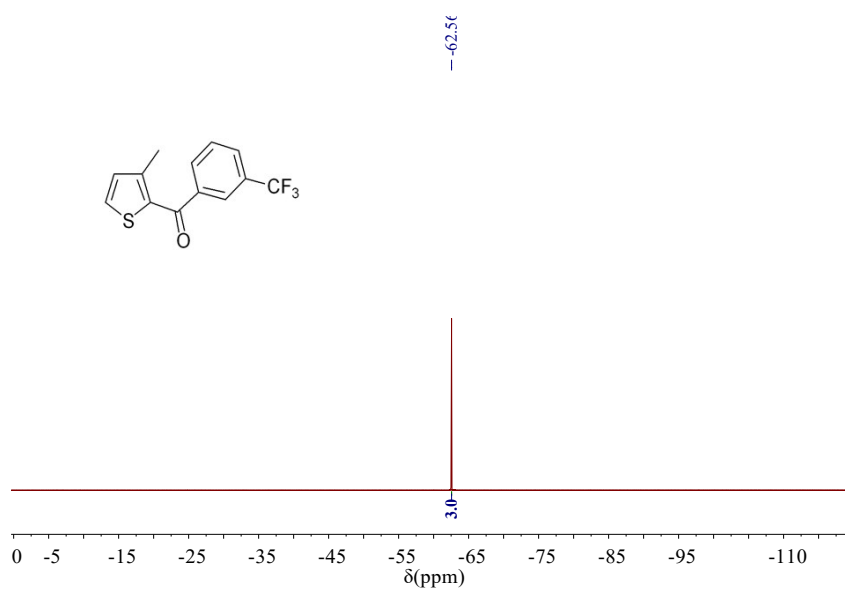
Fig. S1 The PL spectra (a) and emission decay curves (b) of as-prepared complexes in PMMA films at a conc. of 1 wt% at RT.

4. ^1H - and ^{19}F -NMR spectra of all new compounds

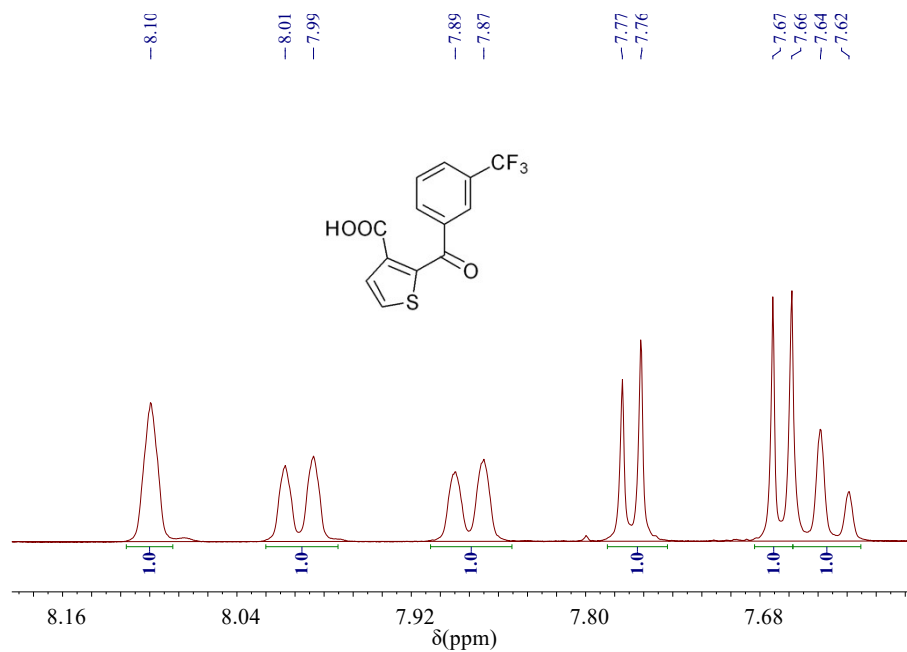
^1H -NMR Spectrum of Z1 in CDCl_3 (400 MHz):



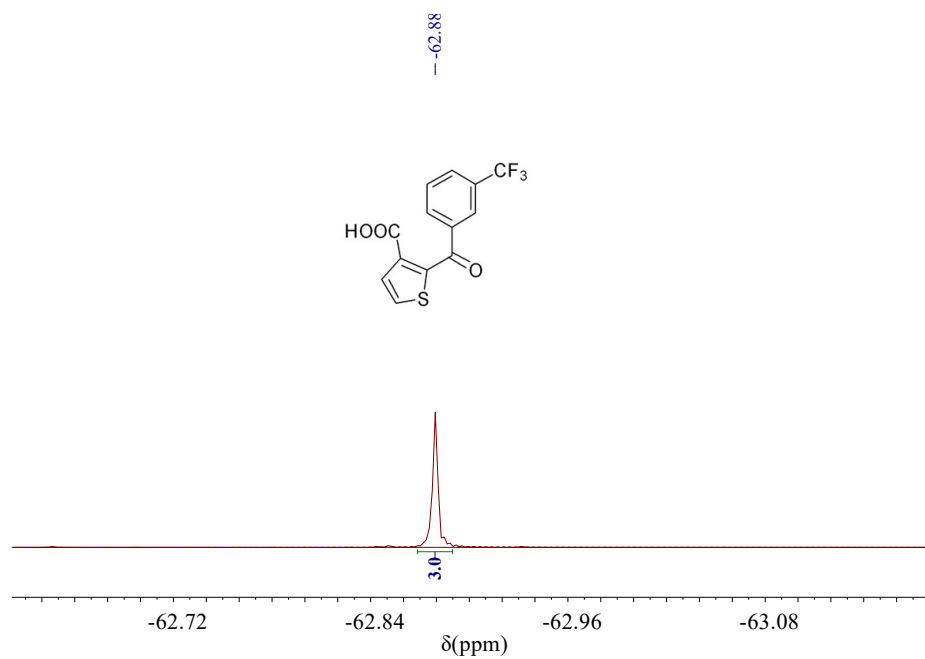
¹⁹F-NMR Spectrum of **Z1** in CDCl₃ (376 MHz):



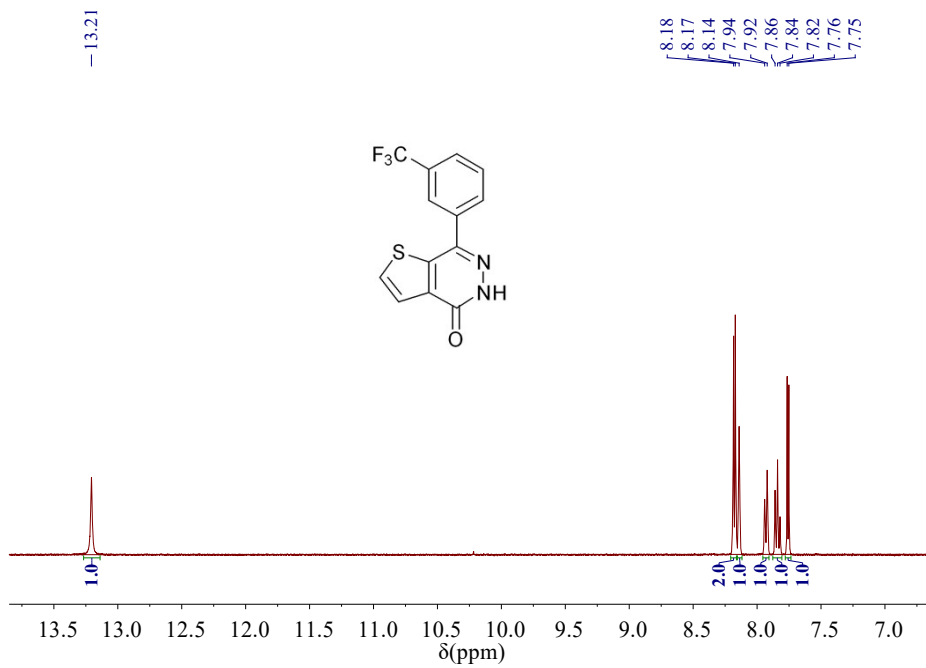
¹H-NMR Spectrum of **Z2** in CDCl₃ (400 MHz):



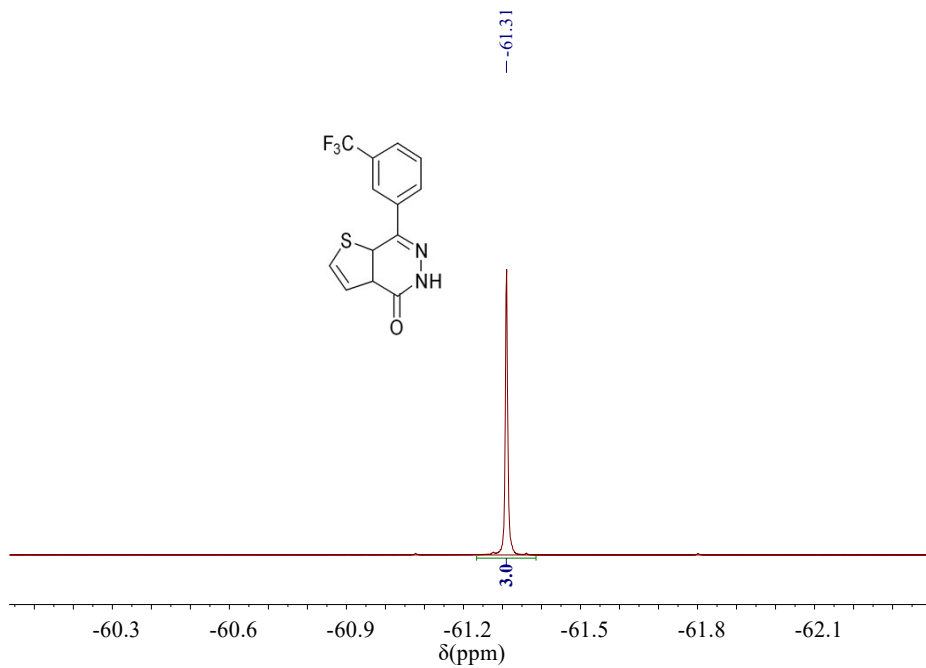
^{19}F -NMR Spectrum of **Z2** in CDCl_3 (376 MHz):



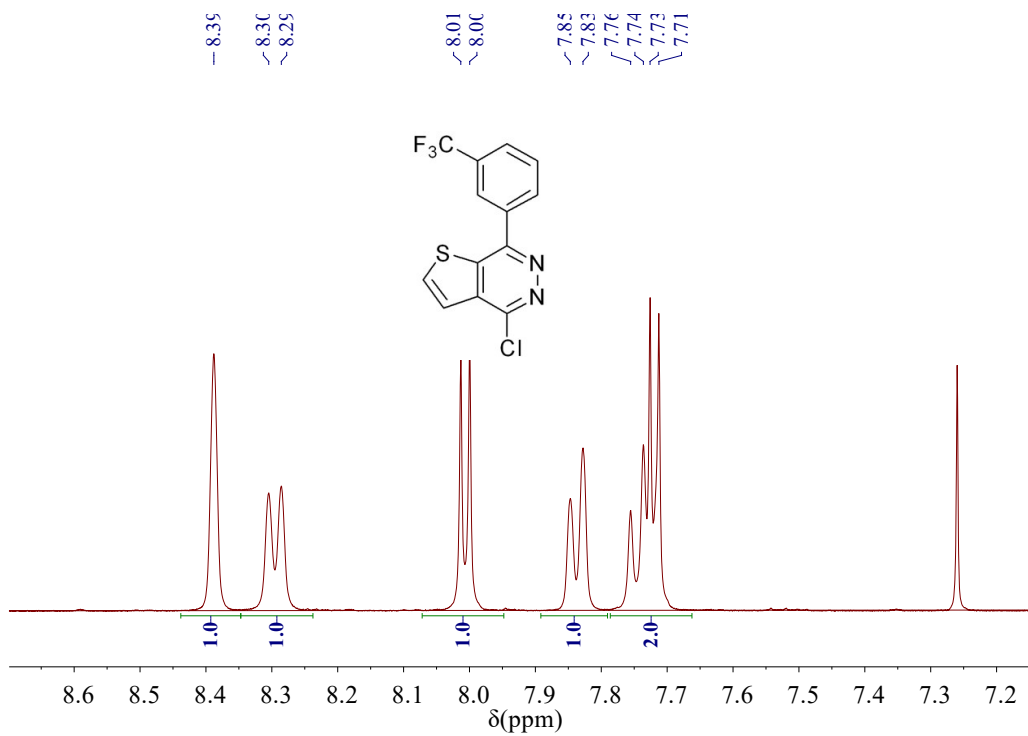
^1H -NMR Spectrum of **Z3** in CDCl_3 (400 MHz):



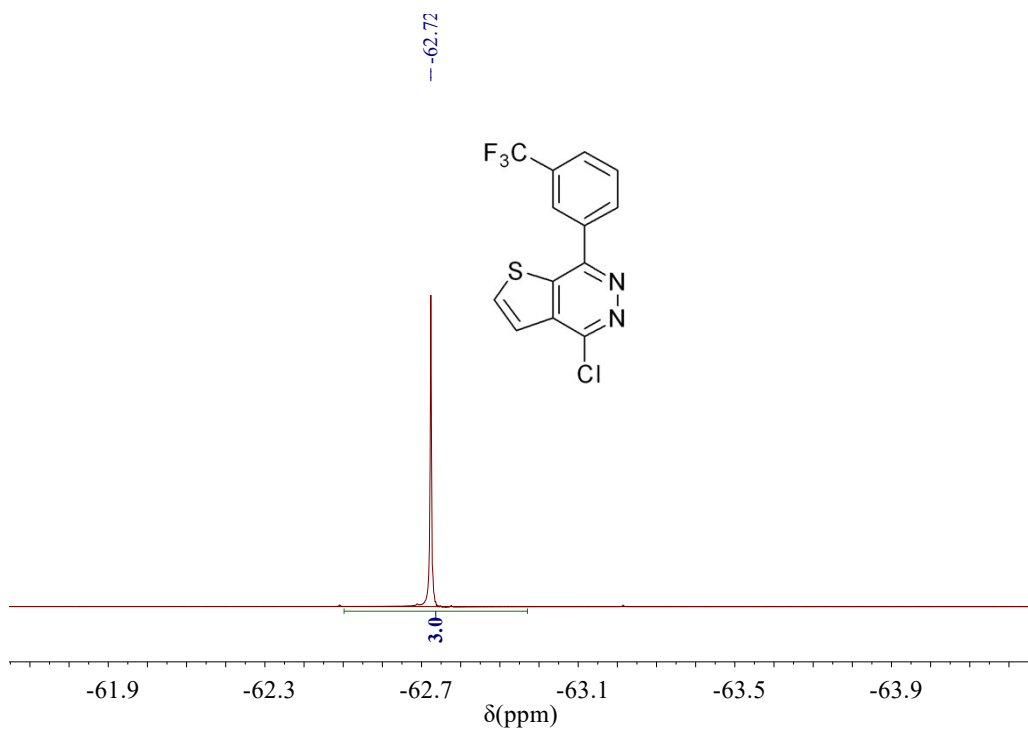
^{19}F -NMR Spectrum of **Z3** in CDCl_3 (376 MHz):



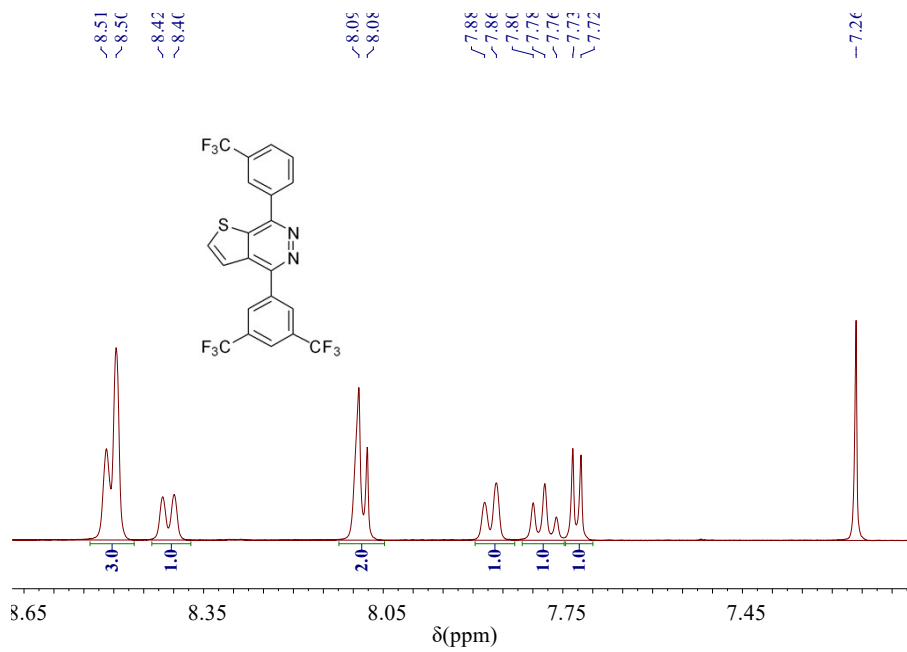
^1H -NMR Spectrum of **Clptp** in CDCl_3 (400 MHz):



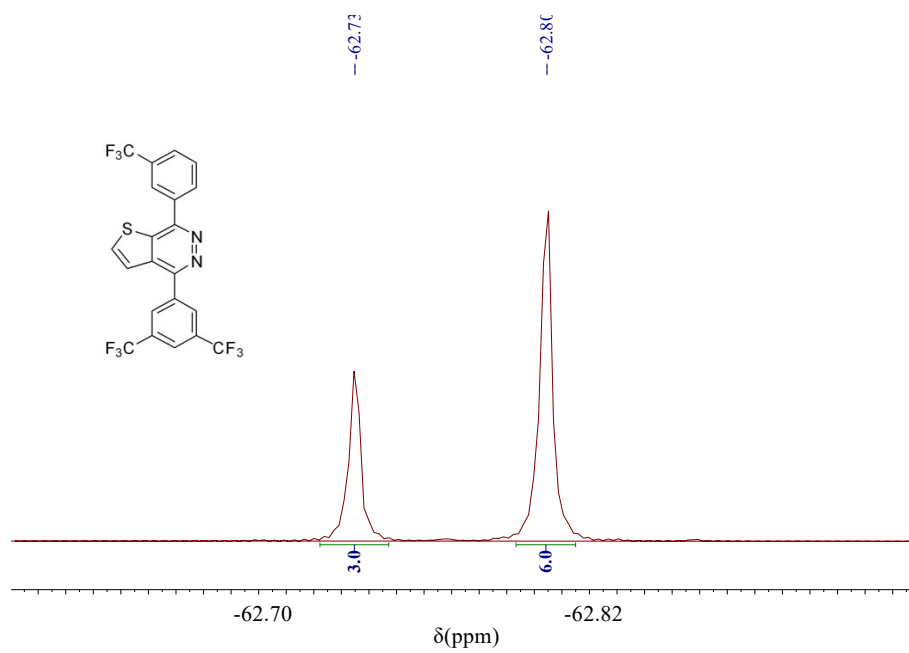
$^{19}\text{F-NMR}$ Spectrum of Clptp in CDCl_3 (376 MHz):



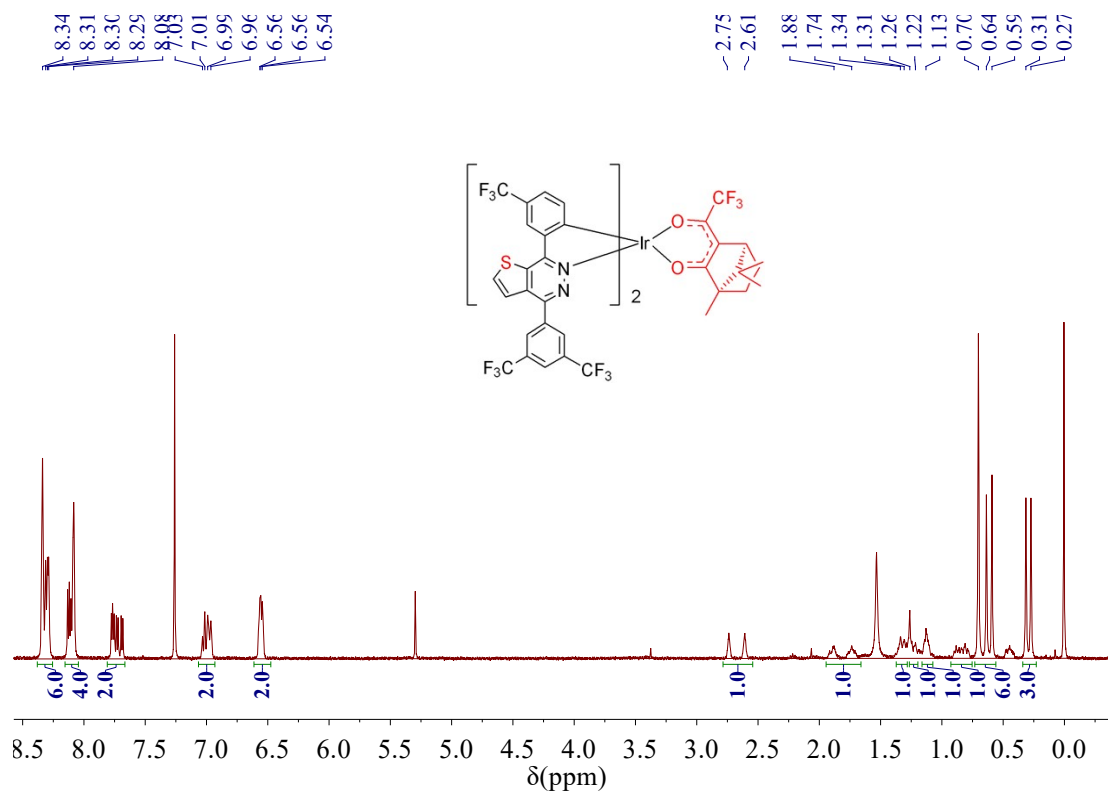
$^1\text{H-NMR}$ Spectrum of ptpH in CDCl_3 (400 MHz):



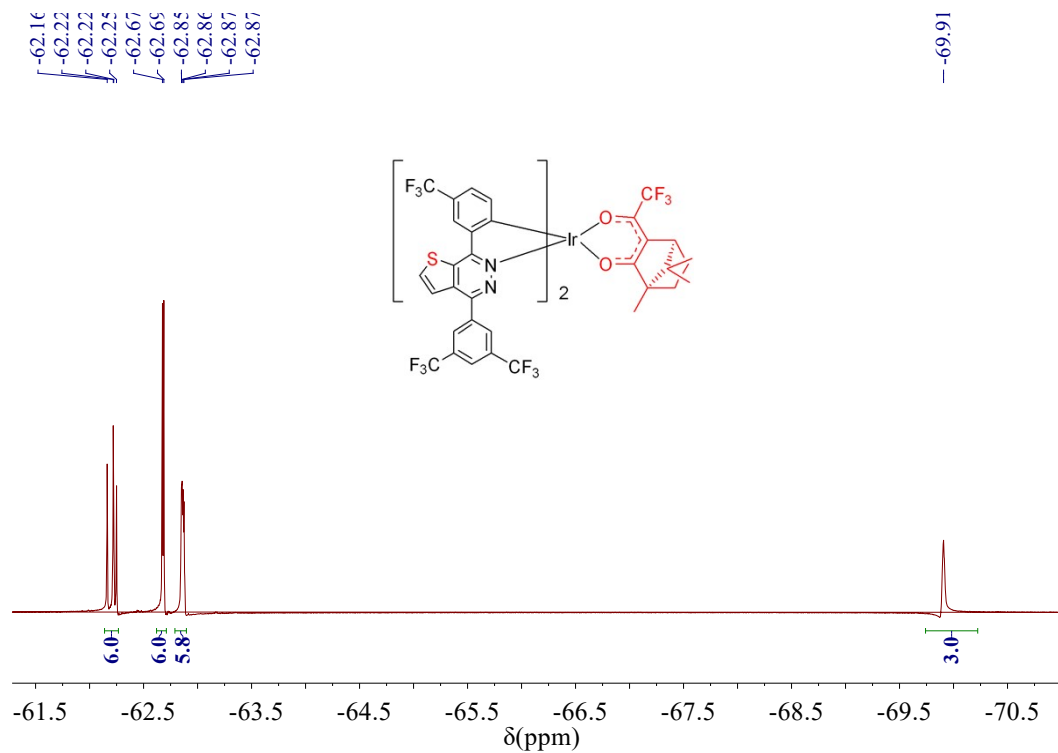
$^{19}\text{F-NMR}$ Spectrum of **ptpH** in CDCl_3 (376 MHz):



$^1\text{H-NMR}$ Spectrum of **IrR** in CDCl_3 (400 MHz):

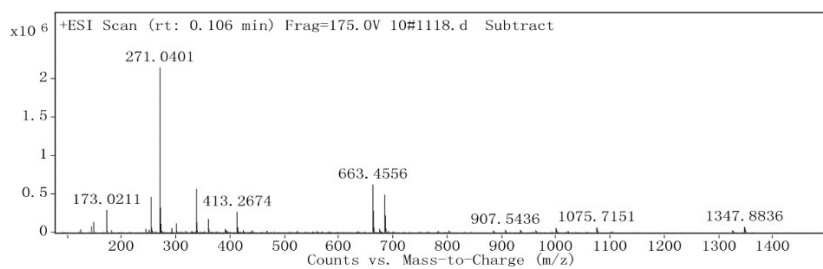


^{19}F -NMR Spectrum of IrR in CDCl_3 (376 MHz):

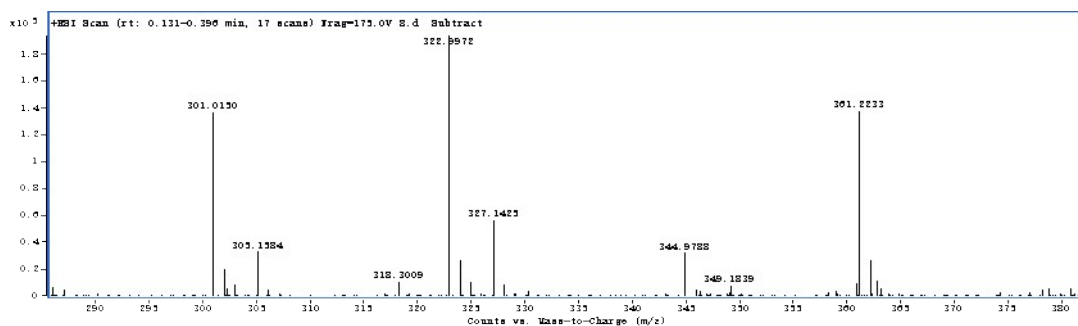


5. High resolution mass spectrometers (HRMS) of all new compounds

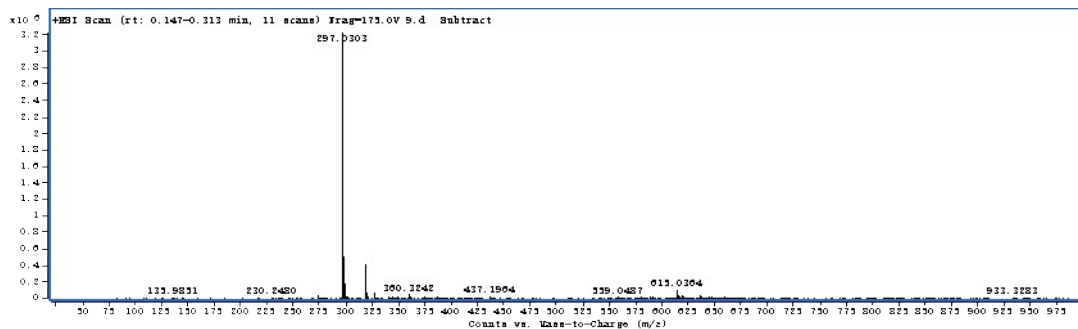
HRMS Spectrum of **Z1**:



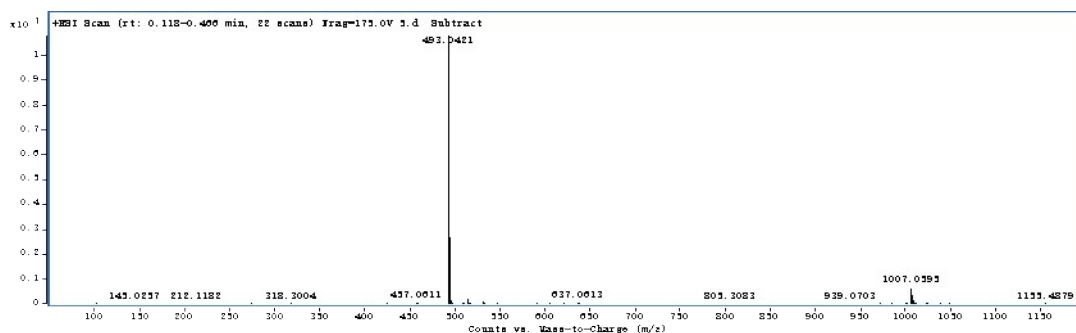
HRMS Spectrum of **Z2**:



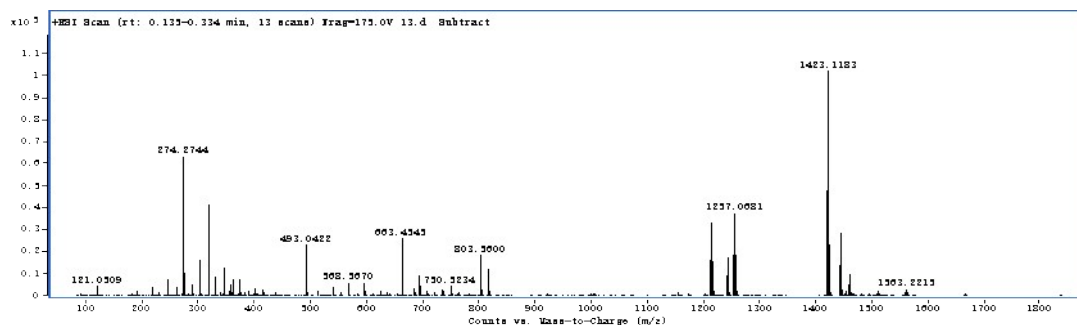
HRMS Spectrum of **Z3**:



HRMS Spectrum of **ptpH**:



HRMS Spectrum of **IrR**:



6. References

- [1] Becke AD. Density-functional thermochemistry. III. The role of exact exchange, *J Chem Phys*, 1993; 98: 5648–5652; b) Lee C, Yang W and Parr RG. Development of the Colic-Salvetti correlation-energy formula into a functional of the electron density. *Phys Rev B*, 1988; 37: 785–789.
- [2] Hay PJ and Wadt WRJ. Ab initio effective core potentials for molecular calculations. Potentials for the transition metal atoms Sc to Hg. *Chem Phys*, 1985; 82: 270–283; b) Wadt WR and Hay PJJ. Ab initio effective core potentials for molecular calculations. Potentials for main group elements Na to Bi. *Chem Phys*, 1985; 82: 284–298; c) Hay PJ and Wadt WR. Ab initio effective core potentials for molecular calculations. Potentials for K to Au including the outermost core orbitals. *J Chem Phys*, 1985; 82: 299–310.
- [3] Hariharan PC and Pople JA. Accuracy of AH n equilibrium geometries by single determinant molecular orbital theory. *Mol Phys*, 1974; 27: 209–214.
- [4] Lu T and Chen FW. Multiwfn: a multifunctional wavefunction analyzer. *J Comput Chem*, 2012; 33: 580–592.
- [5] Humphrey W, Dalke A and Schulten K. VMD - visual molecular dynamics. *J Molec Graphics*, 1996; 14: 33–38.
- [6] Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, et al. *Gaussian 16*, Rev. B.01, Gaussian, Inc., Wallingford CT, 2016.