

Supporting Information

Isomeric effect of thienopyridazine-based iridium complexes

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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 a TOF 5600^{plus} mass spectrometer. X-ray crystallography diffraction was carried out on a Bruker SMART Apex CCD diffractometer. 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.

1.2. Computational methodology

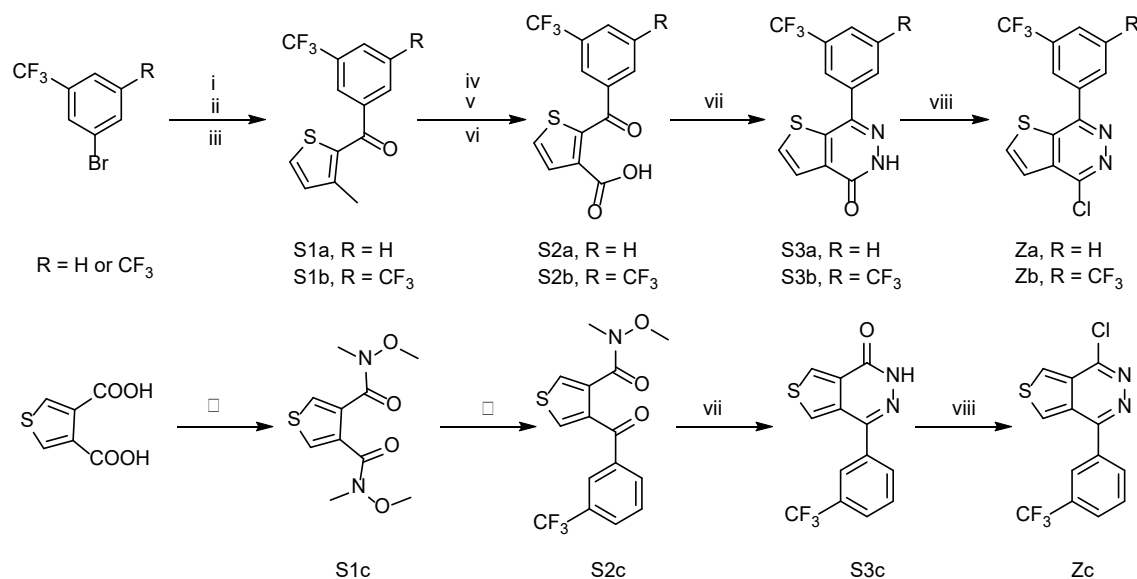
B3LYP functional was used to optimize the geometrical structures of ground state (S_0).^[1] A “double- ξ ” quality basis set consisting of Hay and Wadt’s effective core potentials (ECP), LANL2DZ,^[2] was employed to the Ir atom. 6-31G(d) basis set^[3] was applied to other nonmetallic atoms. The solvent 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 $8 \times 10^{-5} \text{ Pa}$. The organic transport materials were grown by the rate of 0.08-0.15 nm s^{-1} , while organic dopants, AlQ₃ were deposited at the rate of 0.02-0.15 \AA s^{-1} , Al was deposited by the rate of 3 \AA 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.

1.4. Synthetic routes of key intermediates



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, CH_2Cl_2 , r. t., 12 h; iv) NBS, dibenzoyl peroxide, CCl_4 , reflux, 12 h; v) AgNO_3 , ethanol/ H_2O , reflux, 1 h; vi) Jones reagent, acetone, 0 °C, 2 h; vii) Hydrazine hydrate, ethanol, reflux, 12 h; viii) POCl_3 , CHCl_3 , reflux, 12 h. ix) $\text{NHMe}(\text{OMe})$, PCl_3 , toluene, 60 °C, 1.5 h; x) (3-(Trifluoromethyl)phenyl)magnesium bromide, THF, r. t., 2 h.

General preparation process of ketone intermediates. To a solution of Grignard reagents (40 mmol) prepared from brominated aromatic hydrocarbons 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. NH_4Cl (10 mL). The mixture was extracted with EtOAc (3×40 mL). The combined organic extracts were dried with Na_2SO_4 and concentrated in vacuo. The alcohol intermediate crude product was dissolved in CH_2Cl_2 (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 Na_2SO_4 and concentrated in vacuo. Flash column chromatography using petroleum ether/ethyl acetate (V:V=8:1) as the eluent afforded corresponding products.

(3-Methylthiophen-2-yl)(3-(trifluoromethyl)phenyl)methanone (S1a): 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]⁺).

(3,5-Bis(trifluoromethyl)phenyl)(3-methylthiophen-2-yl)methanone (S1b): light yellow liquid, 55%. ¹H NMR (400 MHz, CDCl₃) δ 8.27 (s, 2H), 8.06 (s, 1H), 7.59 (d, $J = 5.0$ Hz, 1H), 7.08 (d, $J = 5.0$ Hz, 1H), 2.54 (s, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ -63.00 (s, 6F). HRMS ((+)-ESI): $m/z = 339.0280$ (calcd. 339.0278 for [C₁₄H₉F₆OS] [M+H]⁺).

General preparation process of keto acid intermediates. A solution of ketone intermediates (1 mmol), NBS (0.53, 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 \times 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 \times 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 corresponding products.

2-(3-(Trifluoromethyl)benzoyl)thiophene-3-carboxylic acid (S2a): 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]⁺).

2-(3,5-Bis(trifluoromethyl)benzoyl)thiophene-3-carboxylic acid (S2b): white solid, 53%. ¹H NMR (400 MHz, CDCl₃) δ 8.23 (s, 2H), 8.09 (s, 1H), 7.68 (q, $J = 5.1$ Hz, 2H). ¹⁹F NMR (376 MHz, CDCl₃) δ -63.02 (s, 6F). HRMS ((+)-ESI): $m/z = 369.0020$ (calcd. 369.0020 for [C₁₄H₇F₆O₃S] [M+H]⁺).

[M+H]⁺.

Synthesis of amide intermediates S1c and S2c.

N³, N⁴-dimethoxy-N³, N⁴-dimethylthiophene-3,4-dicarboxamide (S1c): A solution of NHMe(OMe) (14.17 g, 232.3 mmol) and thiophene-3,4-dicarboxylic acid (4.00 g, 23.2 mmol) was stirred in dry toluene (150 mL) at 0 °C for 10 min. PCl₃ (4.79 g, 34.9 mmol) was then added dropwise to the mixture. The mixture was warmed to r.t. slowly and then stirred at 60 °C for 1.5 h. Then the mixture was cooled to r.t. and quenched with saturated NaHCO₃ aqueous solution and extracted with EtOAc. The combined organic layers were dried and the solvent was removed in vacuum to give the pure product (5.73 g, 87%) as light yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 7.78 (s, 2H), 3.51 (s, 6H), 3.29 (s, 6H). HRMS ((+)-ESI): m/z = 281.0608 (calcd. 281.0572 for [C₁₀H₁₄N₂NaO₄S] [M+Na]⁺).

N-methoxy-N-methyl-4-(3-(trifluoromethyl)benzoyl)thiophene-3-carboxamide (S2c): To a solution of Grignard reagent (10.0 mmol) prepared from 3-bromotrifluoromethylbenzene and magnesium in dry THF (15 mL), the solution of S1c (0.50 g, 2.0 mmol) in dry THF (5 mL) was added at 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 × 10 mL). The combined organic extracts were dried (Na₂SO₄) and concentrated in vacuo. Flash column chromatography using CH₂Cl₂/EtOAc as the eluent afforded S2c (0.47g, 65%) as white solid. ¹H NMR (400 MHz, CDCl₃) δ 8.08 (s, 1H), 7.99 (d, *J* = 7.2 Hz, 1H), 7.81 (d, *J* = 7.2 Hz, 1H), 7.75 (d, *J* = 2.9 Hz, 1H), 7.72 (d, *J* = 3.1 Hz, 1H), 7.60 (t, *J* = 7.8 Hz, 1H), 3.44 (s, 3H), 3.12 (s, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ -62.75 (s, 3F). HRMS ((+)-ESI): m/z = 366.0383 (calcd. 366.0388 for [C₁₀H₁₂F₃NNaO₃S] [M+Na]⁺).

General preparation process of pyridazinone intermediates. A solution of keto acid intermediates (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 was filtered and washed with ethanol, then dried in an oven.

7-(3-(Trifluoromethyl)phenyl)thieno[2,3-*d*]pyridazin-4(5*H*)-one (S3a): 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, CDCl₃) δ -61.31 (s, 3F). HRMS ((+)-ESI): m/z = 297.0303 (calcd. 297.0309 for [C₁₃H₈F₃N₂OS] [M+H]⁺).

7-(3,5-Bis(trifluoromethyl)phenyl)thieno[2,3-*d*]pyridazin-4(5*H*)-one (S3b): yellow solid, 81%. ¹H

NMR (400 MHz, DMSO-*d*6) δ 13.32 (s, 1H), 8.48 (s, 2H), 8.34 (s, 1H), 8.18 (d, $J = 5.2$ Hz, 1H), 7.77 (d, $J = 5.2$ Hz, 1H). ^{19}F NMR (376 MHz, CDCl_3) δ -61.42 (s, 3F), -61.43 (s, 3F). HRMS ((+)-ESI): $m/z = 365.0181$ (calcd. 365.0183 for $[\text{C}_{14}\text{H}_7\text{F}_6\text{N}_2\text{OS}] [\text{M}+\text{H}]^+$).

4-(3-(Trifluoromethyl)phenyl)thieno[3,4-*d*]pyridazin-1(2*H*)-one (S3c): white solid, 70%. ^1H NMR (400 MHz, DMSO-*d*6) δ 12.39 (s, 1H), 8.70 (d, $J = 3.2$ Hz, 1H), 8.28 (d, $J = 2.8$ Hz, 1H), 8.08 (d, $J = 6.8$ Hz, 1H), 8.01 (s, 1H), 7.89 (d, $J = 6.8$ Hz, 1H), 7.79 (t, $J = 7.2$ Hz, 1H). ^{19}F NMR (376 MHz, DMSO-*d*6) δ -61.14 (s, 3F). HRMS ((+)-ESI): $m/z = 297.0320$ (calcd. 297.0309 for $[\text{C}_{13}\text{H}_8\text{F}_3\text{N}_2\text{OS}] [\text{M}+\text{H}]^+$).

General preparation process of chloro intermediates. A solution of pyridazinone intermediates (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 \times 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 corresponding products.

4-Chloro-7-(3-(trifluoromethyl)phenyl)thieno[2,3-*d*]pyridazine (Za): 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).

4-(3,5-Bis(trifluoromethyl)phenyl)-7-chlorothieno[2,3-*d*]pyridazine (Zb): white solid, 88%. ^1H NMR (400 MHz, CDCl_3) δ 8.61 (s, 2H), 8.09 (s, 1H), 8.05 (d, $J = 5.5$ Hz, 1H), 7.76 (d, $J = 5.4$ Hz, 1H). ^{19}F NMR (376 MHz, CDCl_3) δ -62.91 (s, 6F).

1-Chloro-4-(3-(trifluoromethyl)phenyl)thieno[3,4-*d*]pyridazine (Zc): yellow solid, 59%. ^1H NMR (400 MHz, CDCl_3) δ 8.37 (d, $J = 3.0$ Hz, 1H), 8.23 (d, $J = 3.1$ Hz, 1H), 8.20 (s, 1H), 8.14 (d, $J = 7.6$ Hz, 1H), 7.83 (d, $J = 7.6$ Hz, 1H), 7.72 (t, $J = 7.6$ Hz, 1H). ^{19}F NMR (376 MHz, CDCl_3) δ -62.64 (s, 3F).

2. Photophysical properties

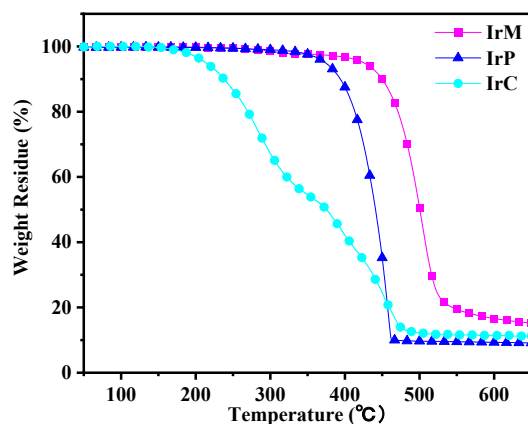


Fig. S1 Thermal gravimetric spectra of as-prepared complexes.

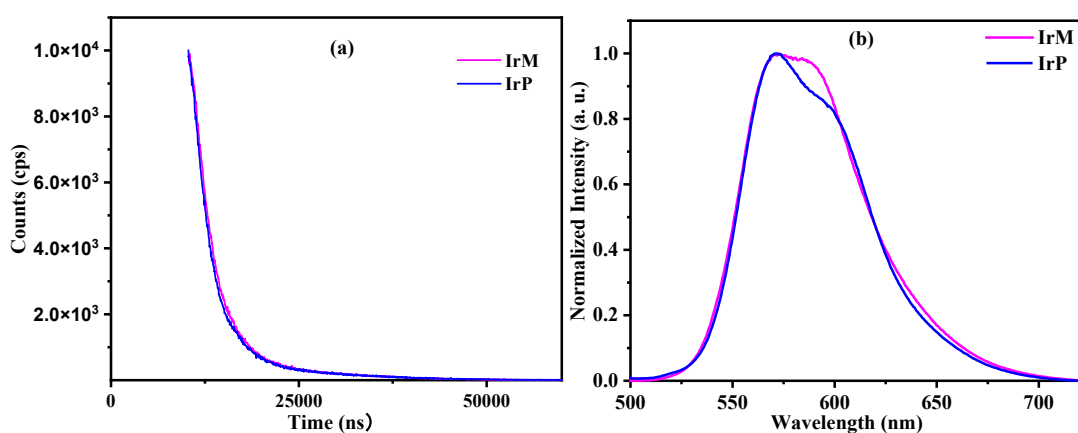


Fig. S2 The emission decay curves (a) of complexes IrM and IrP in PMMA films at a conc. of 1 wt%, and the PL spectra (b) of complexes IrM and IrP in powders.

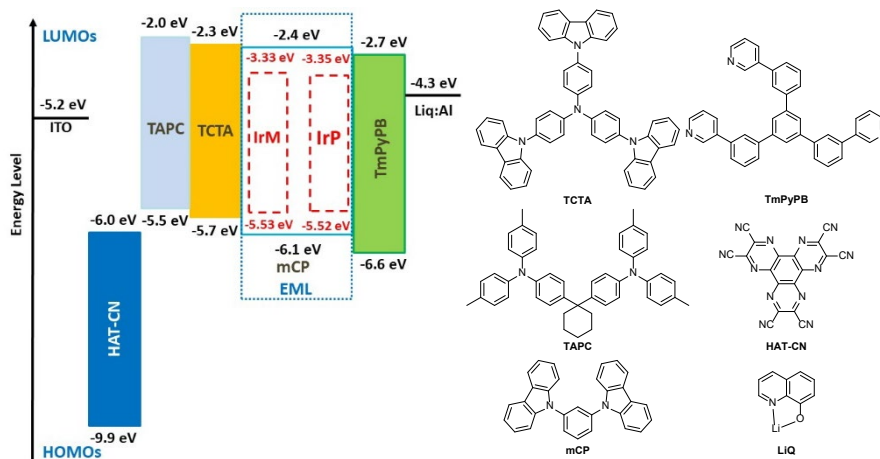
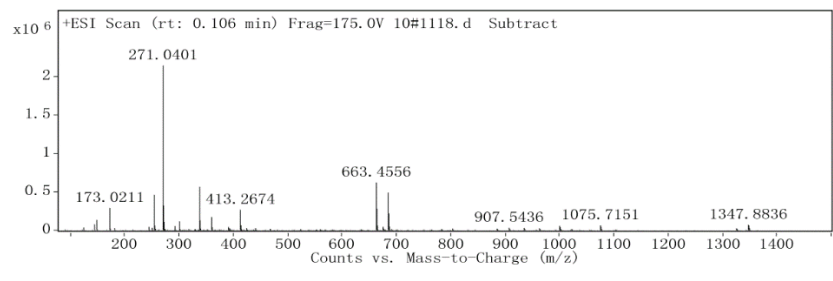
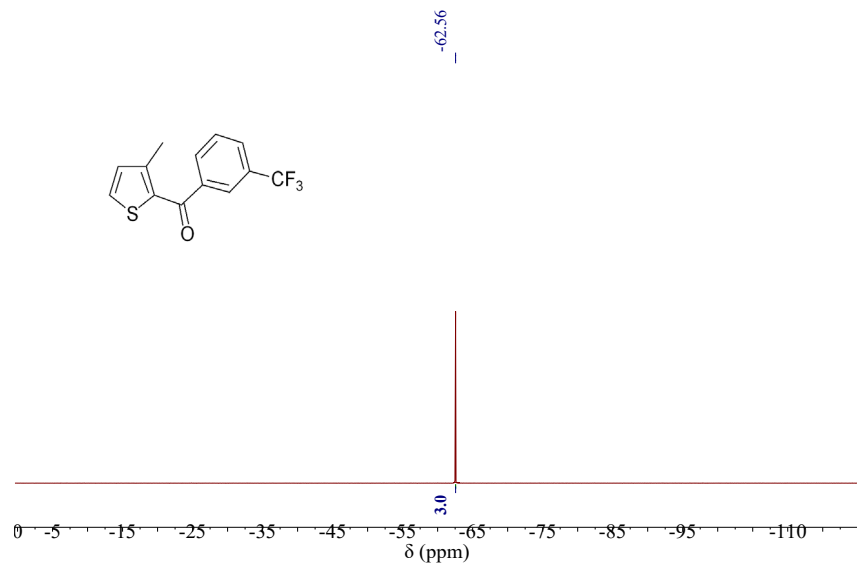
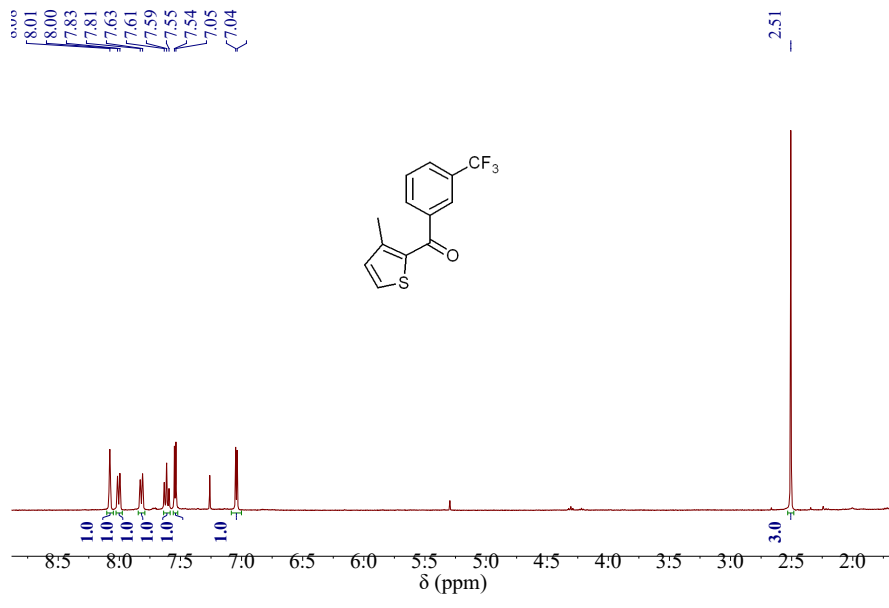


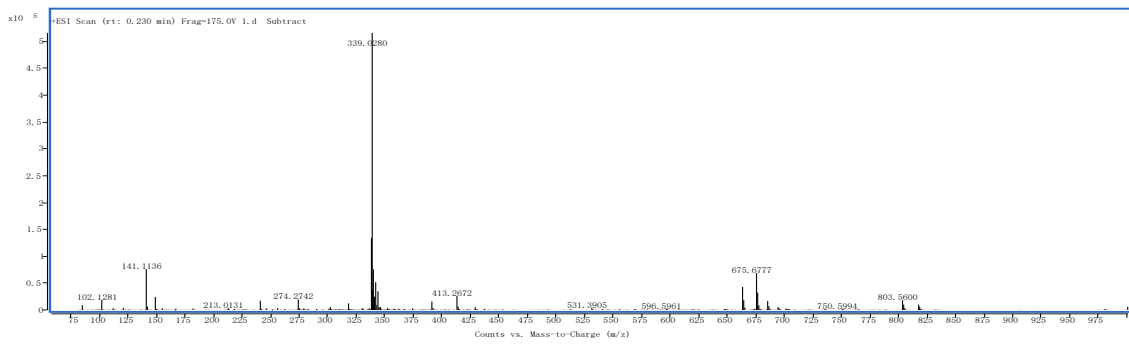
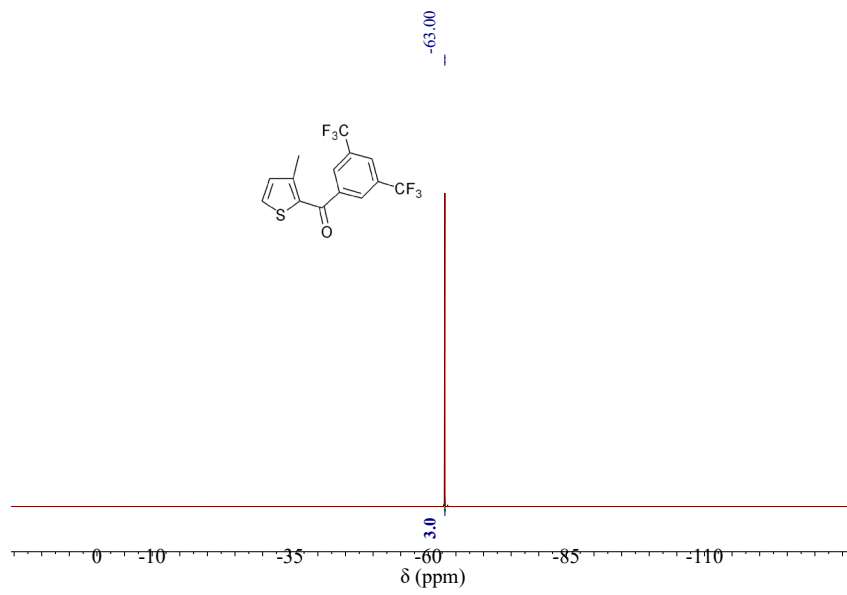
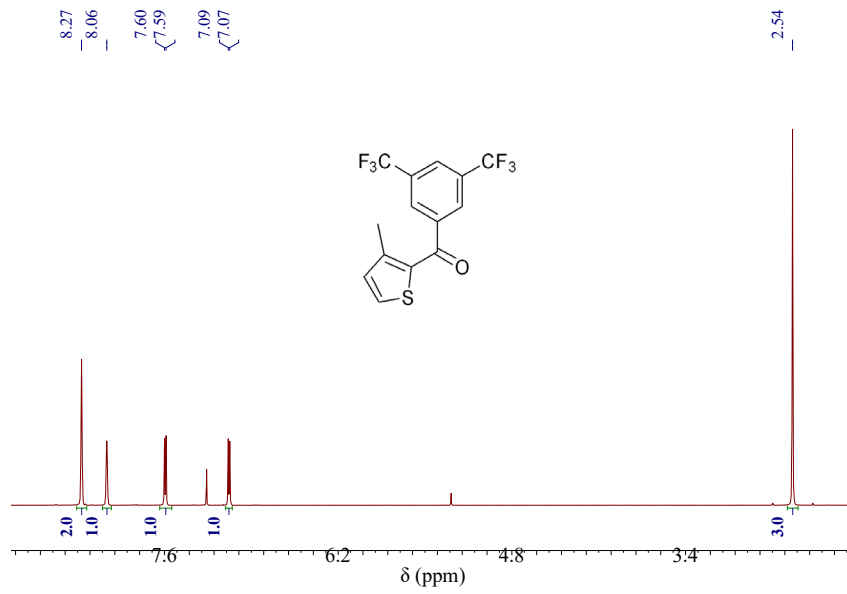
Fig. S3 The device configurations and the energy level diagrams of used materials.

3. The $^1\text{H}/^{19}\text{F}$ NMR and high resolution mass spectrometers (HRMS) spectra of all new compounds.

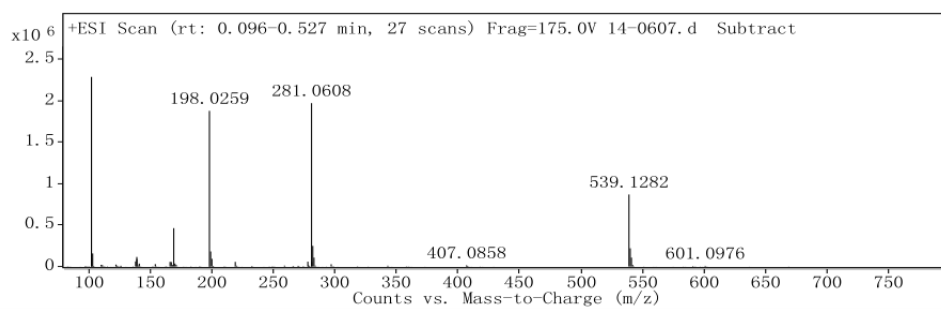
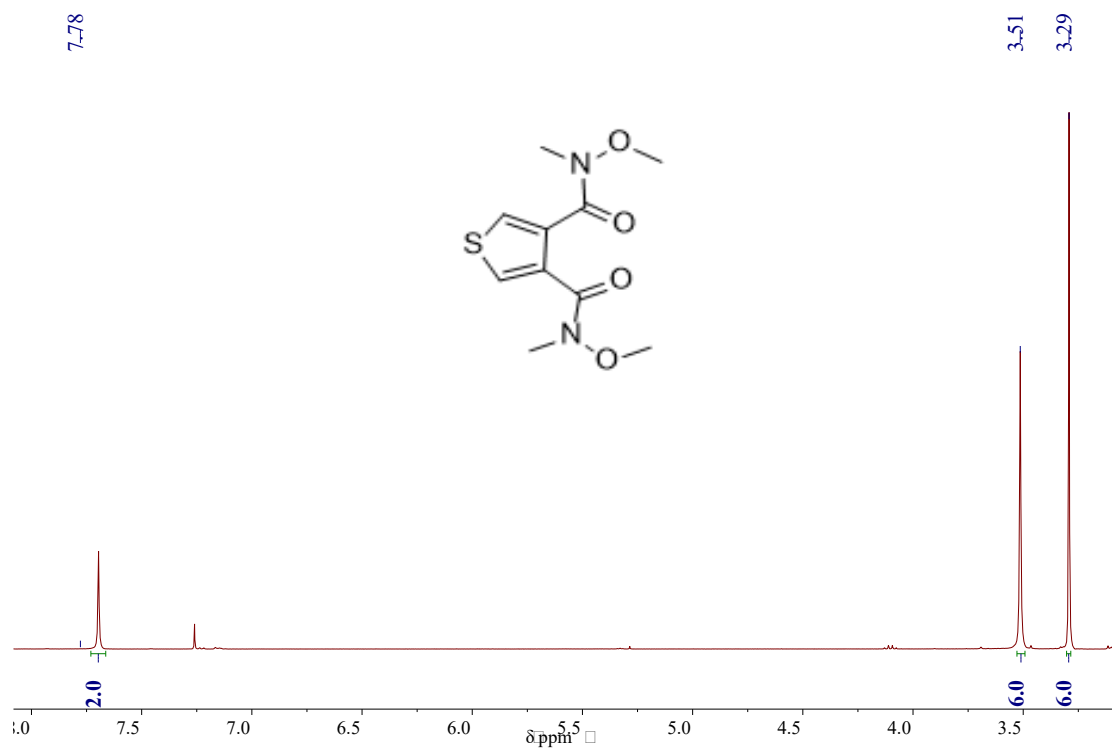
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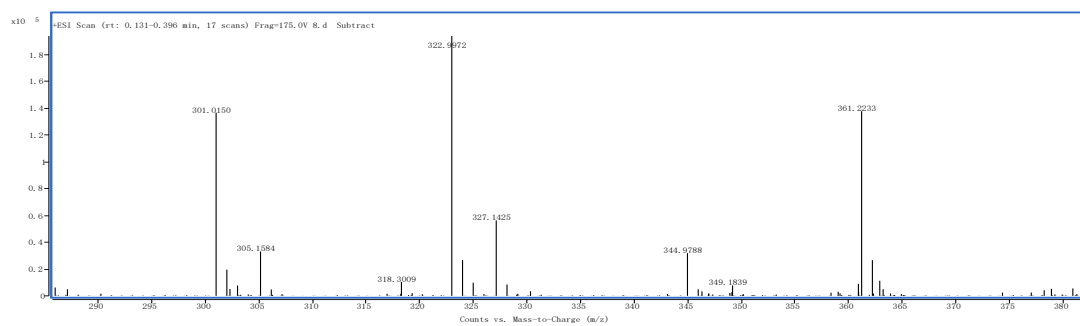
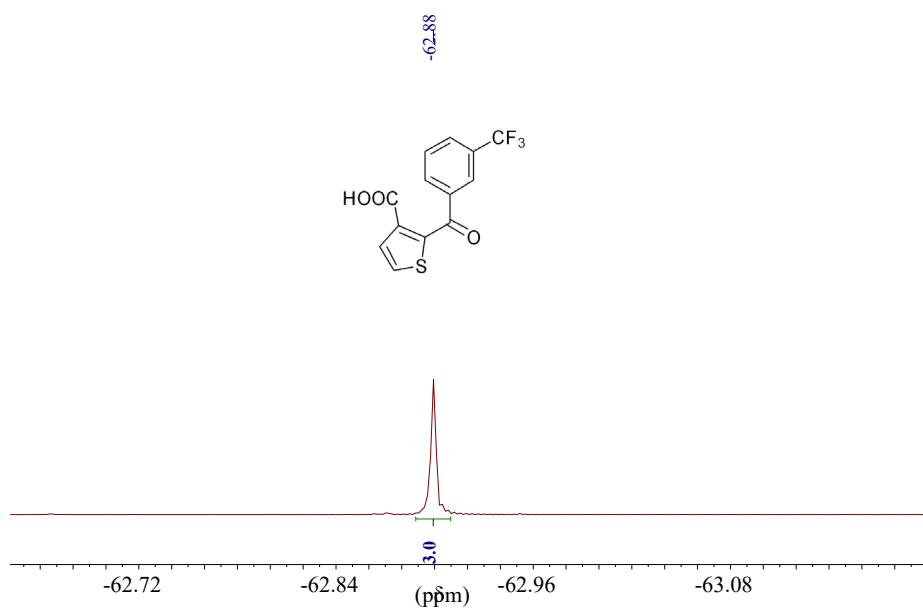
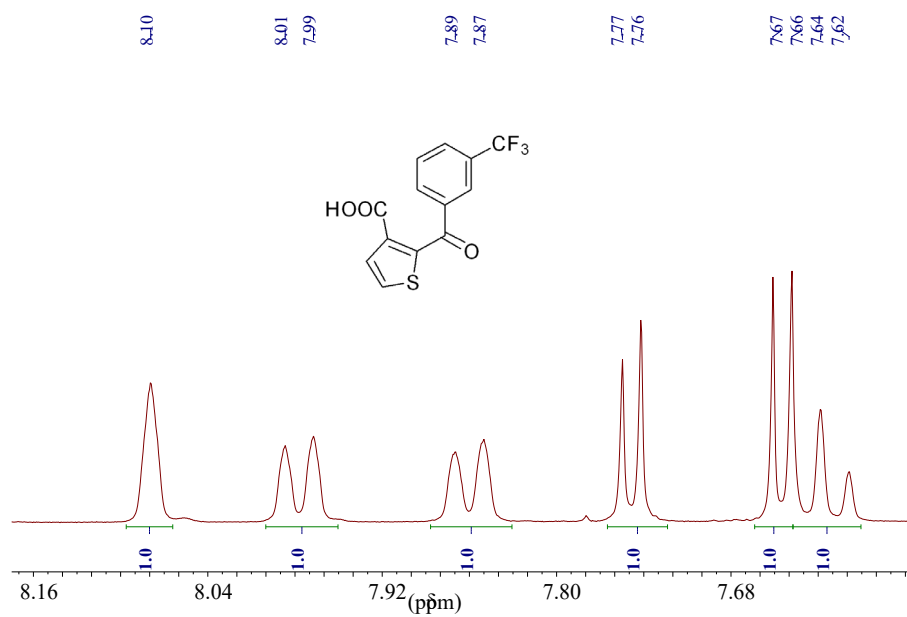
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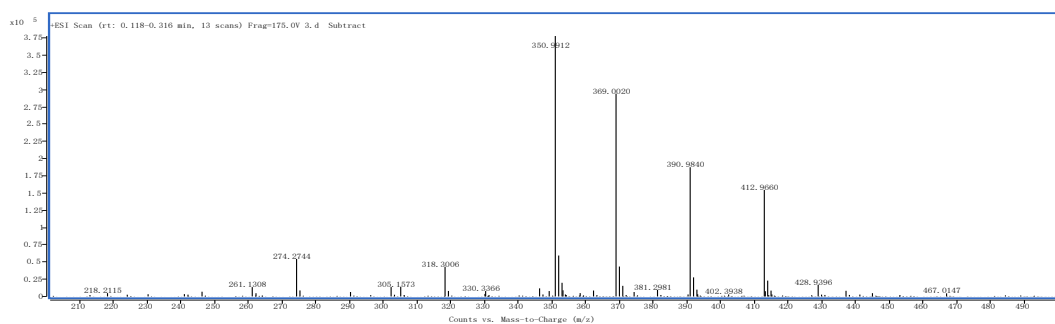
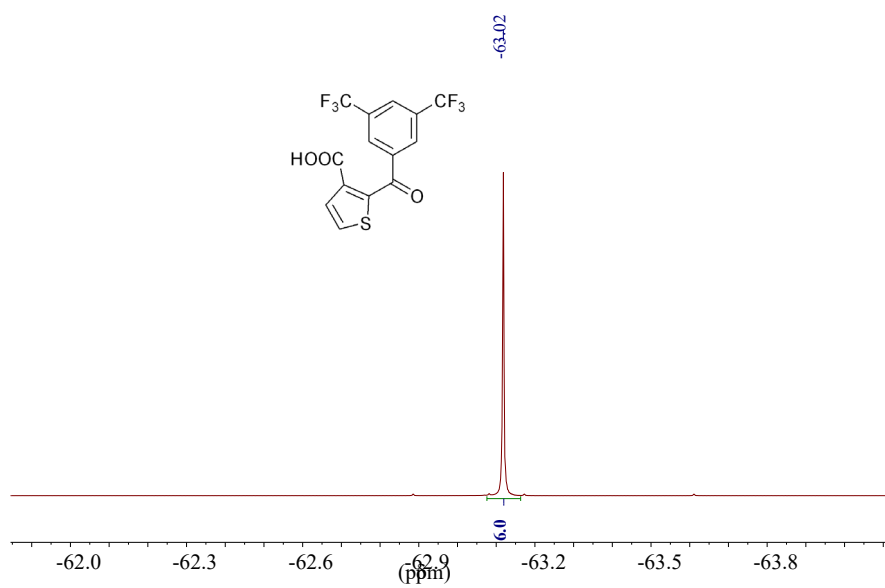
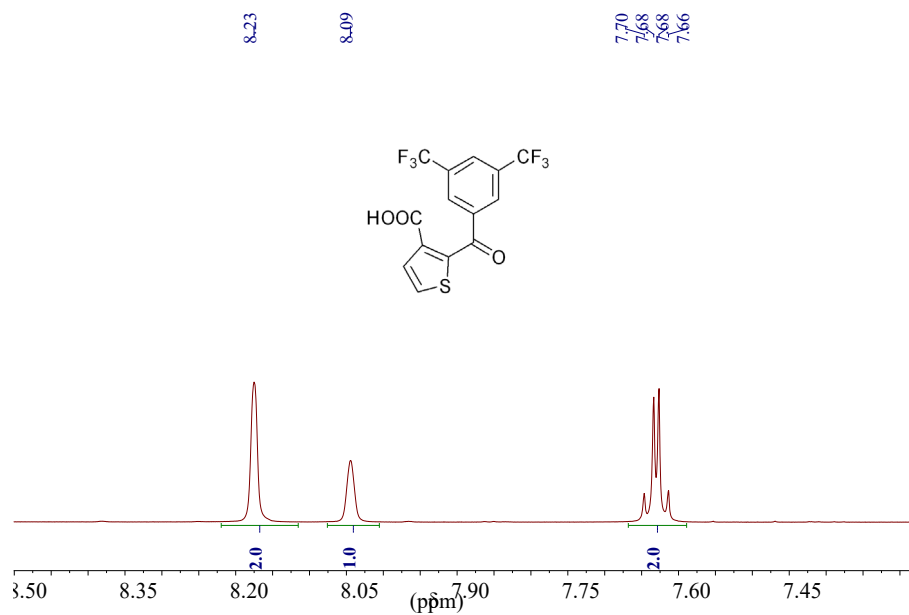
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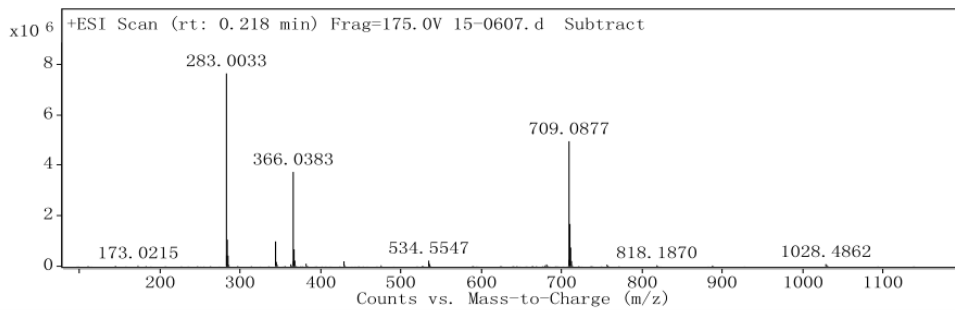
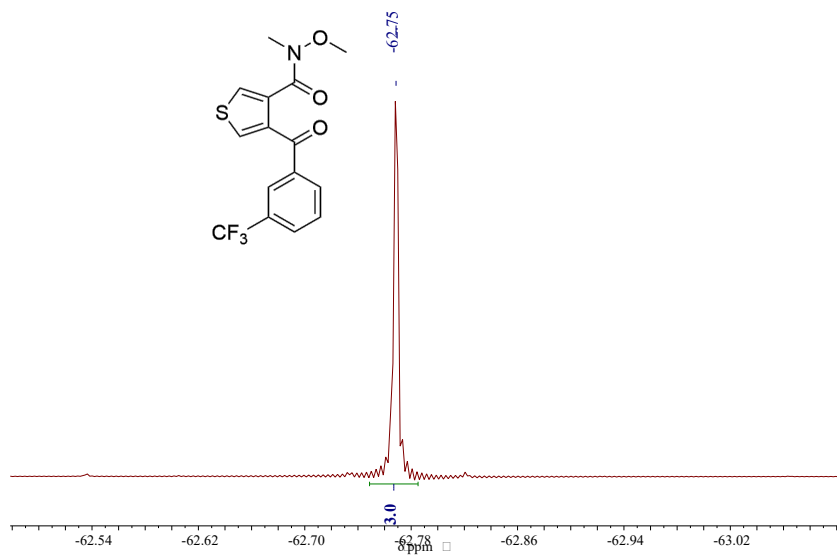
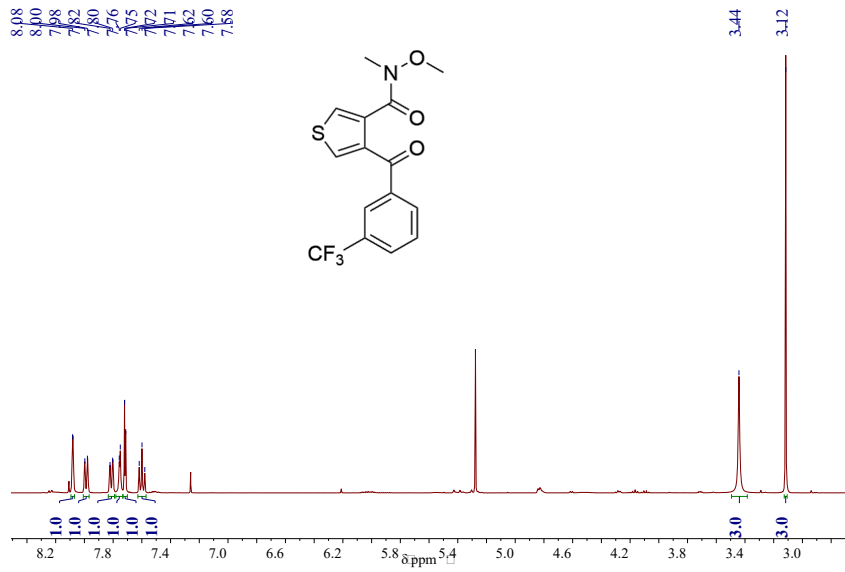
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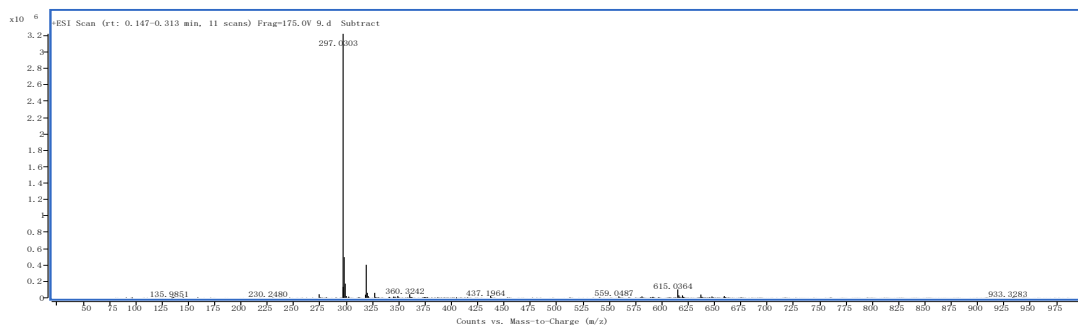
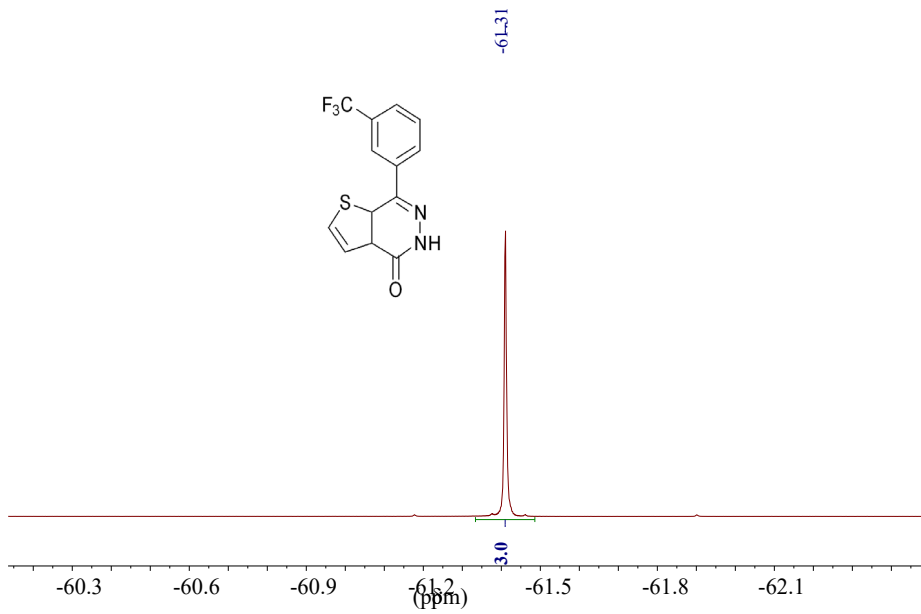
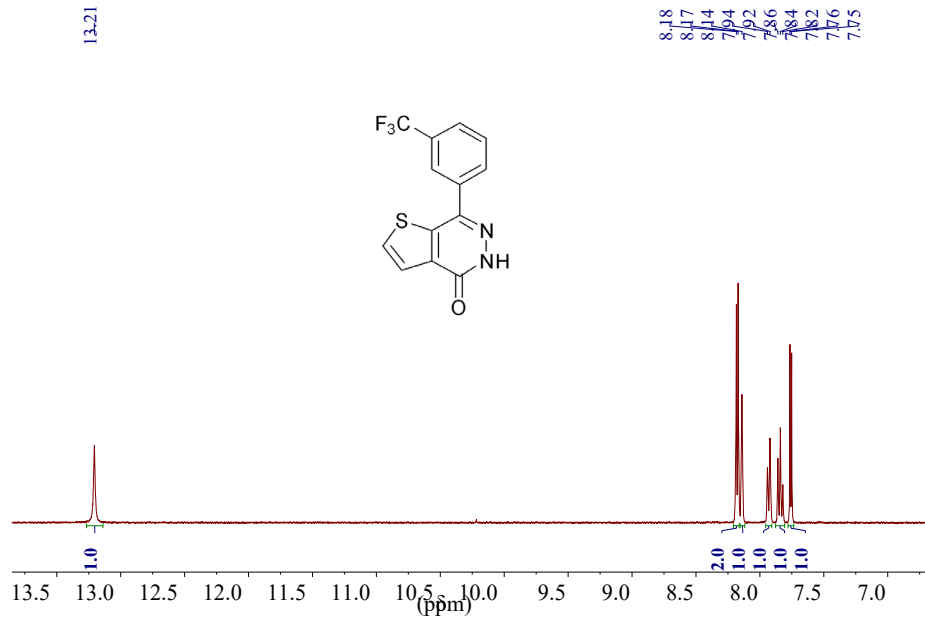
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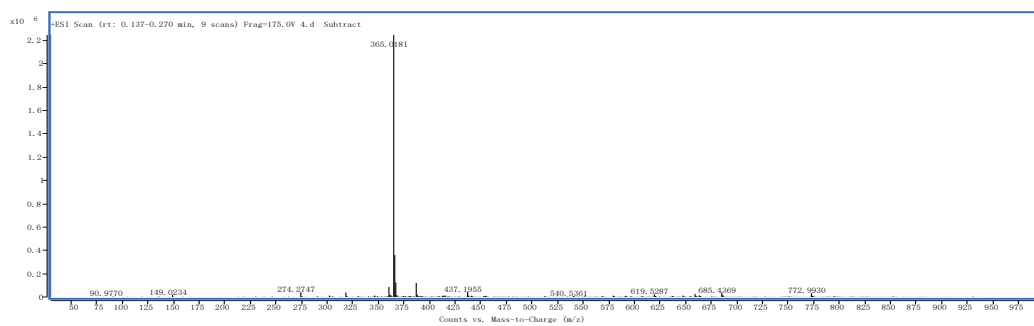
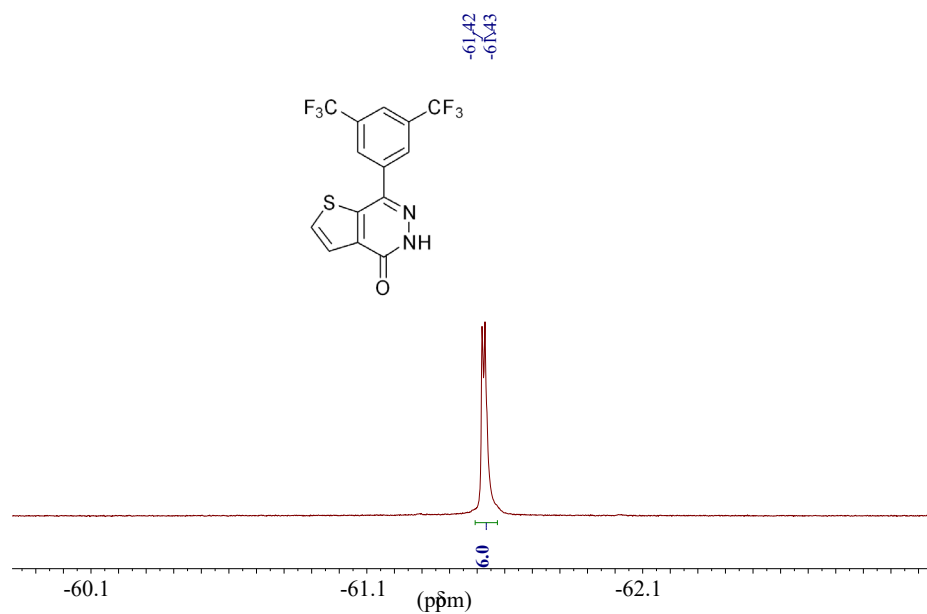
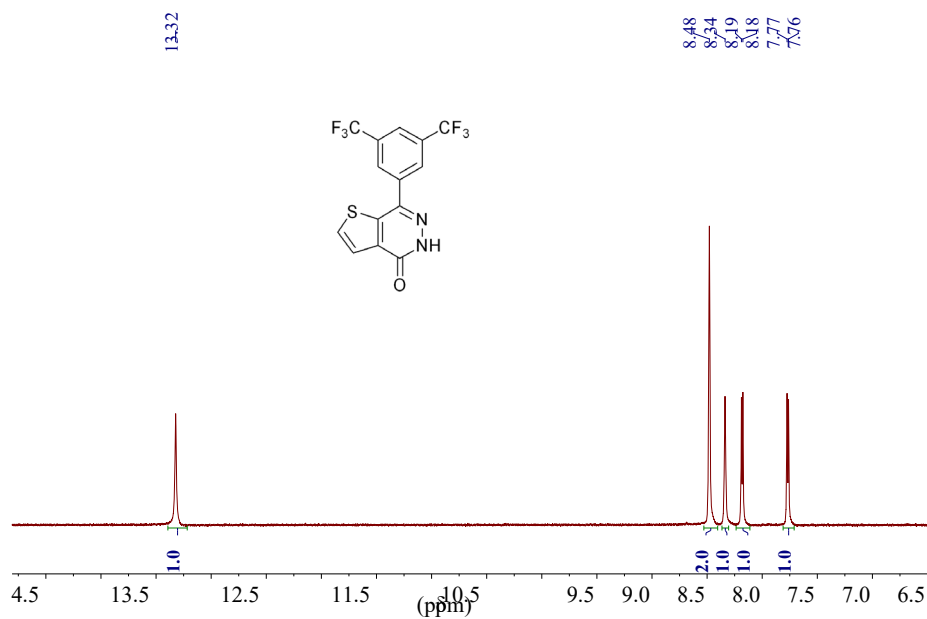
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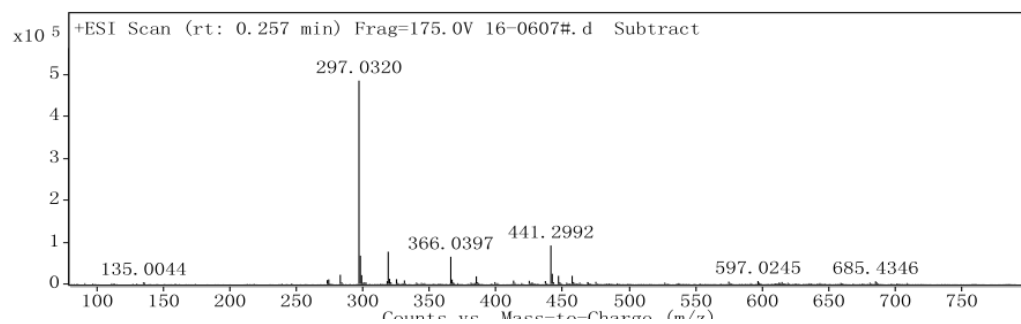
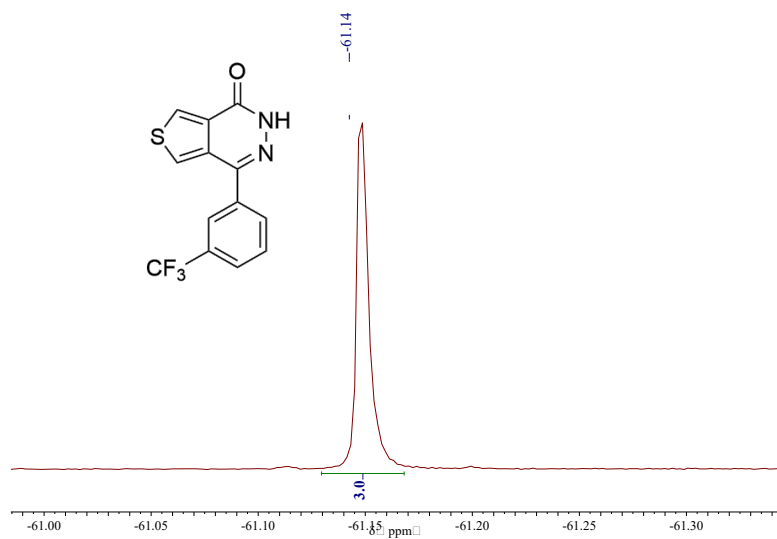
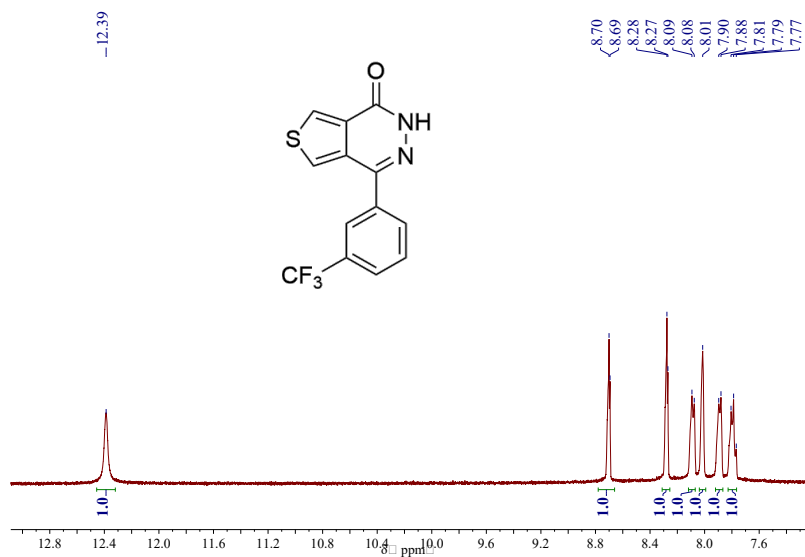
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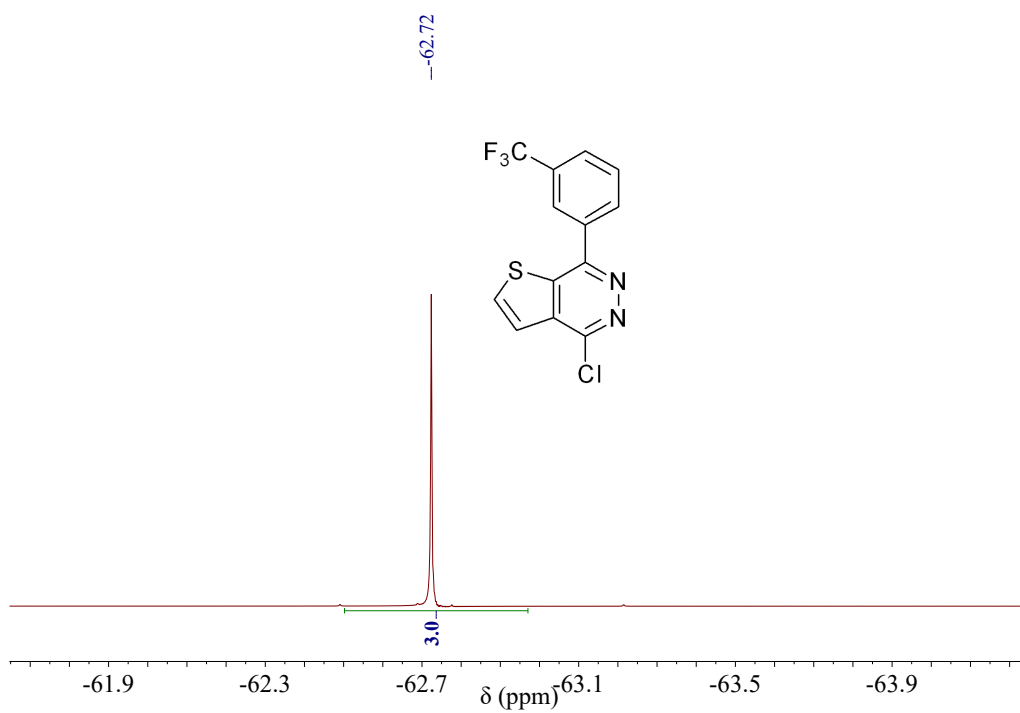
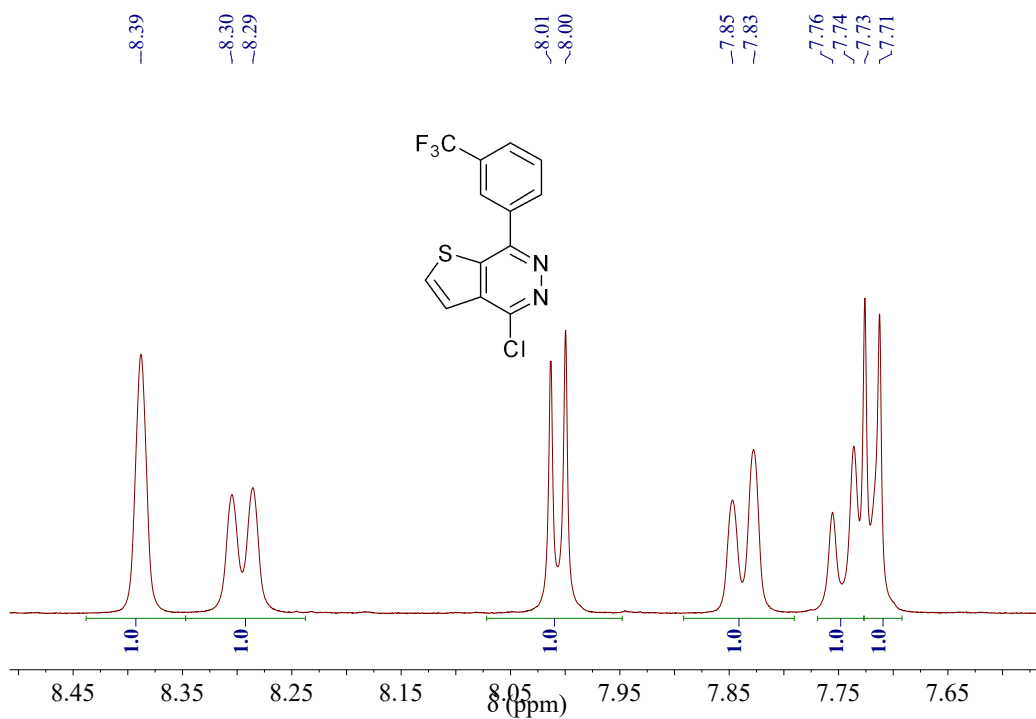
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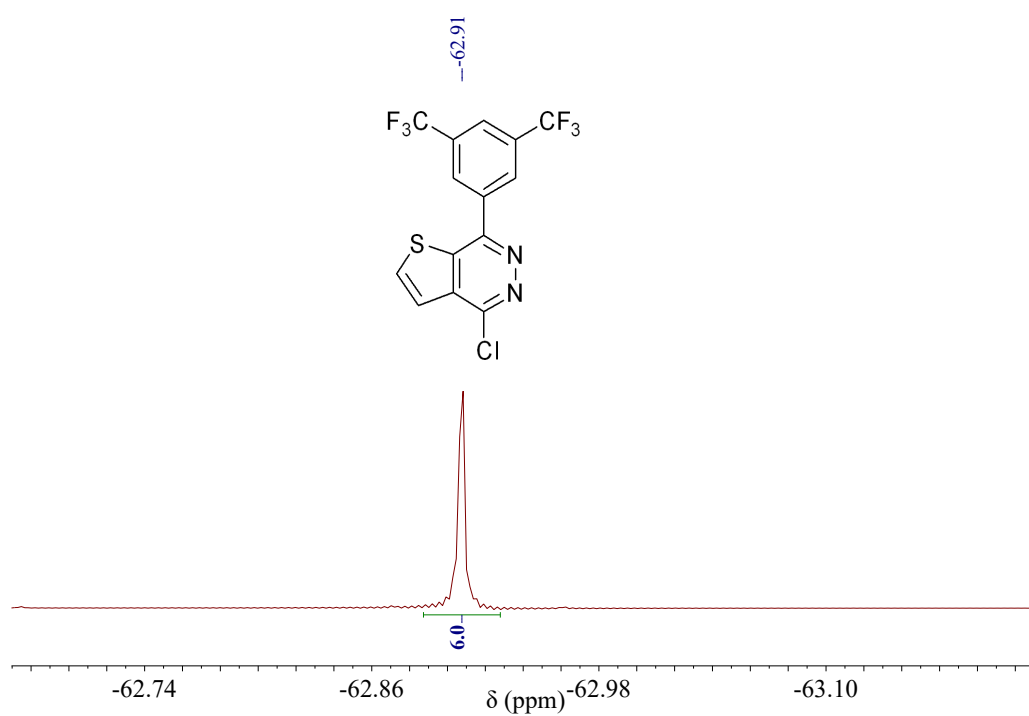
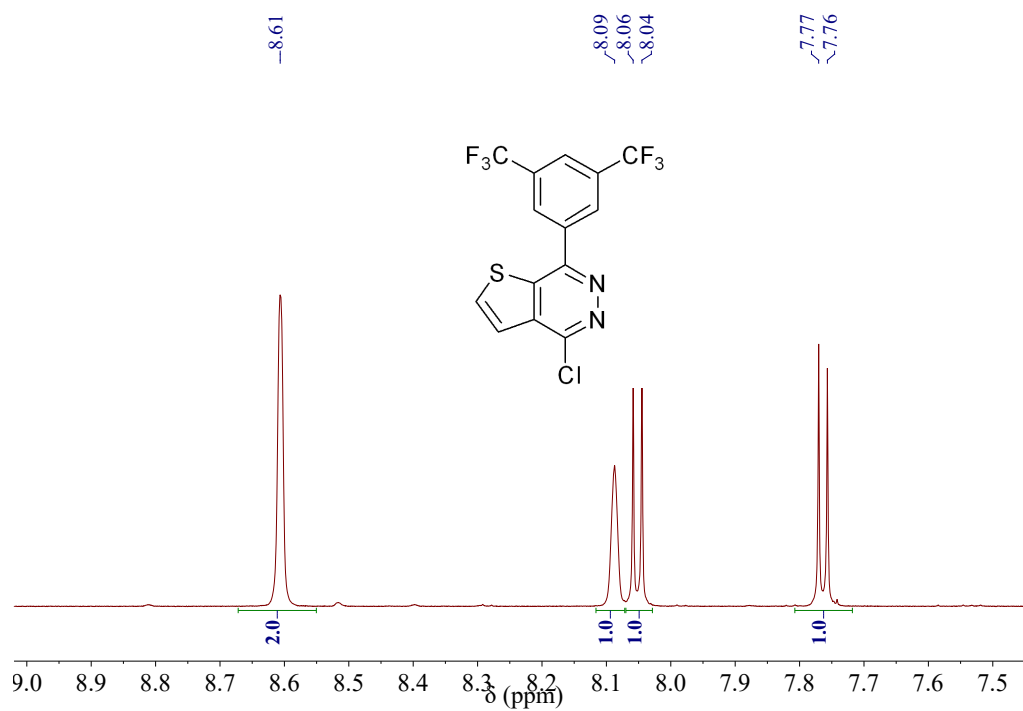
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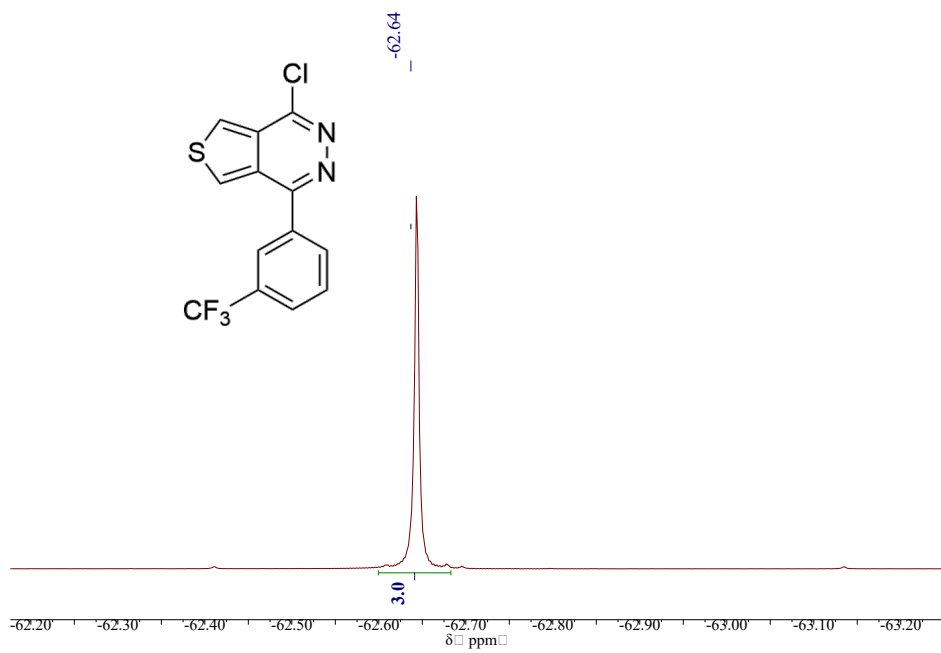
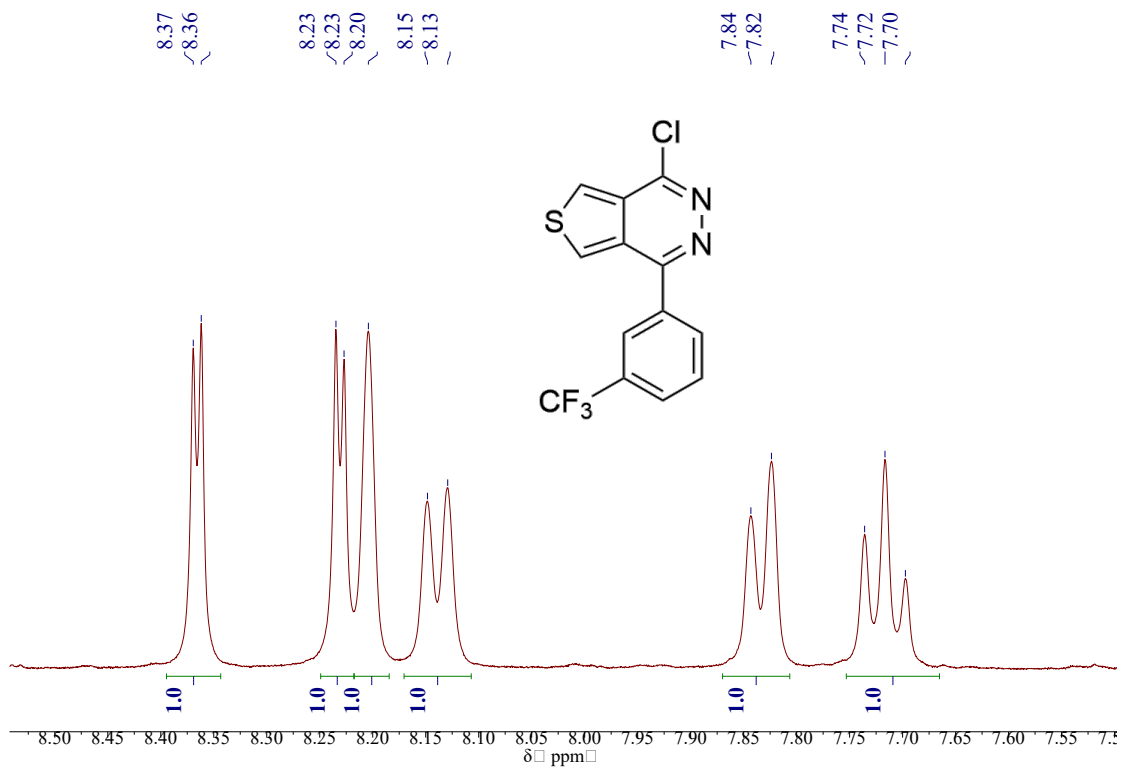
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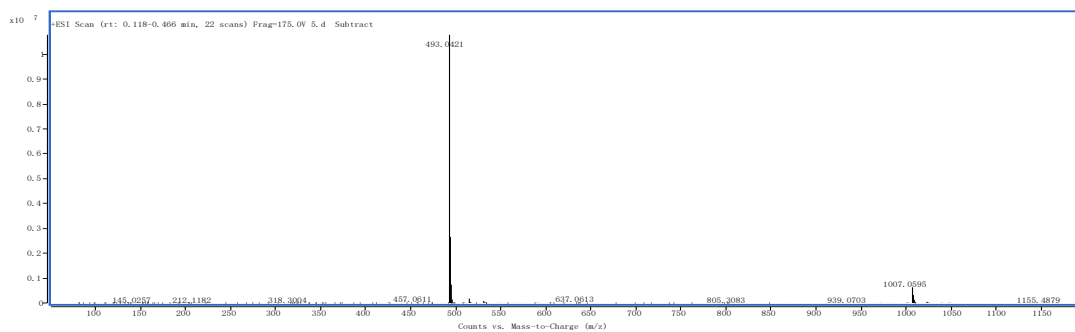
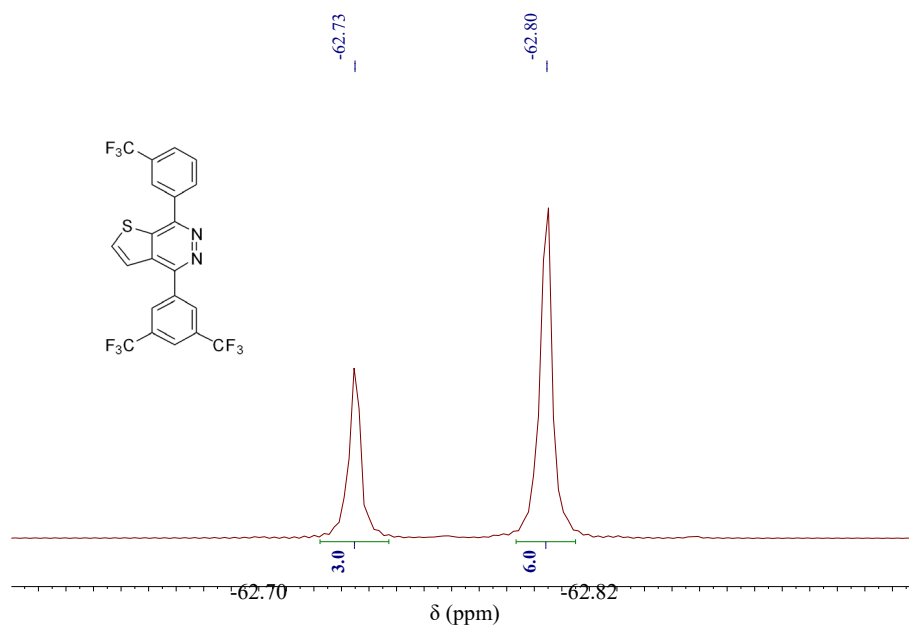
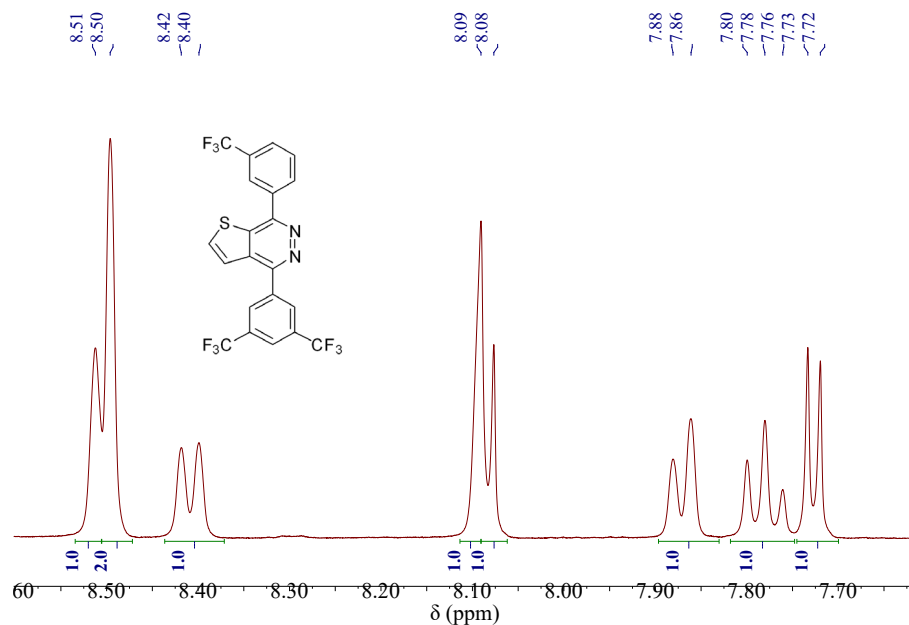
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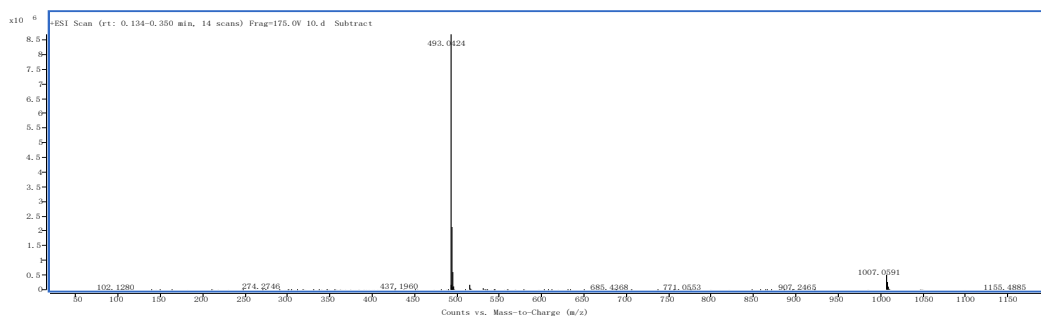
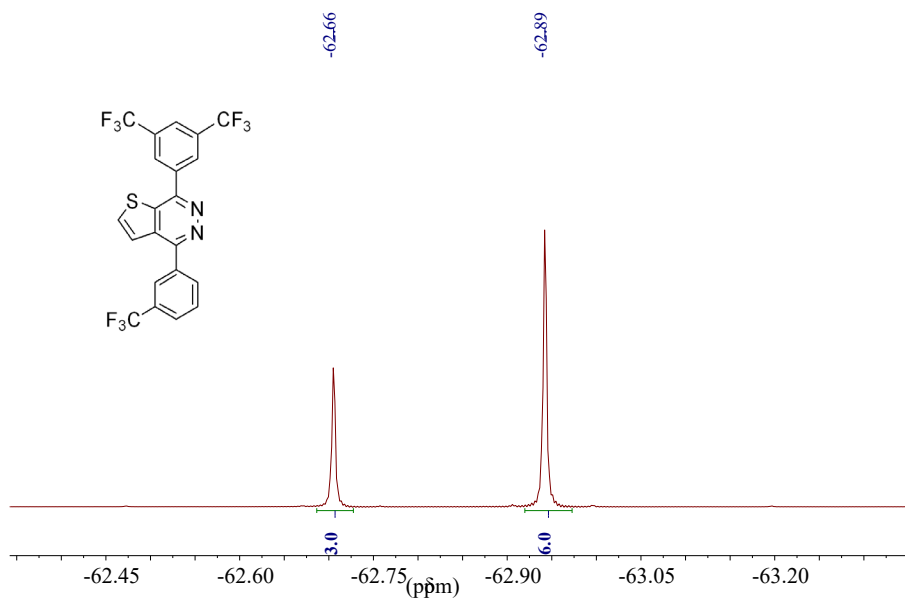
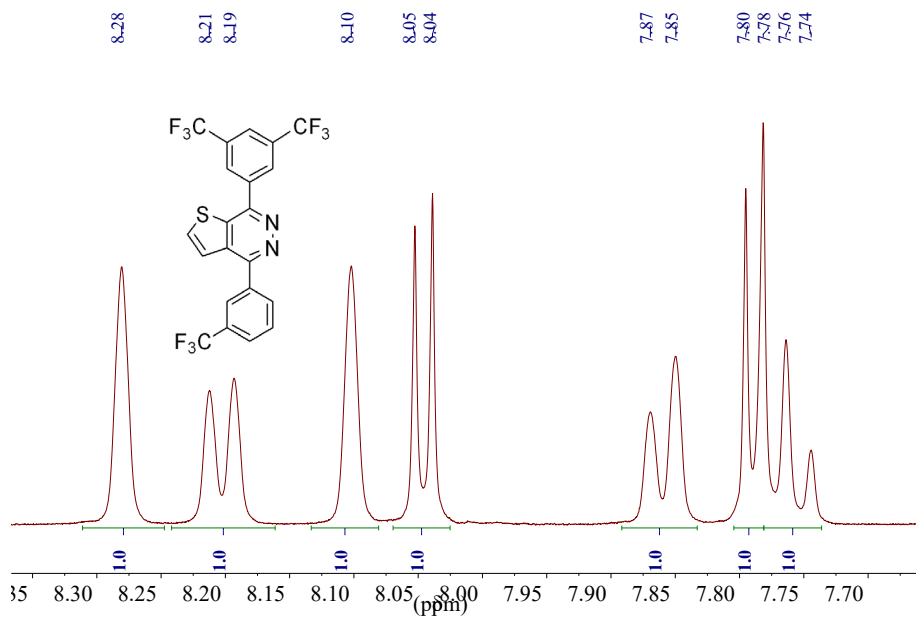
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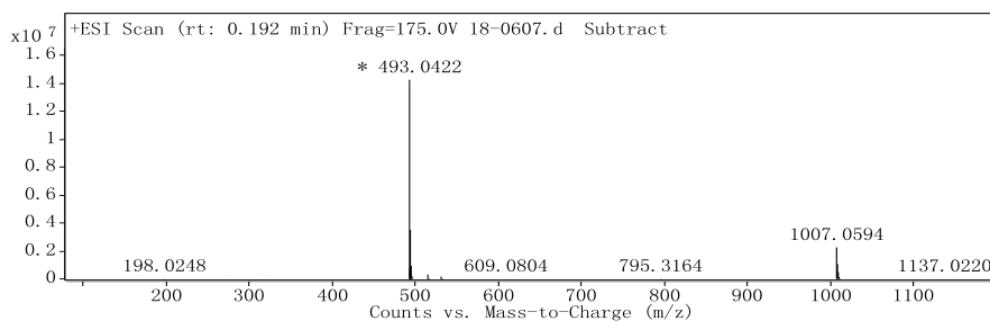
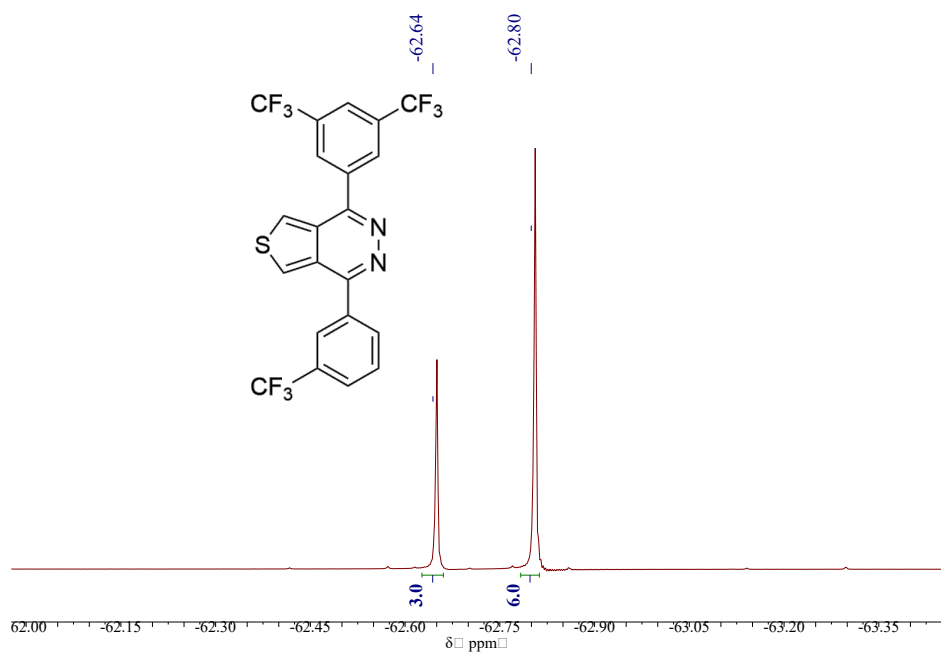
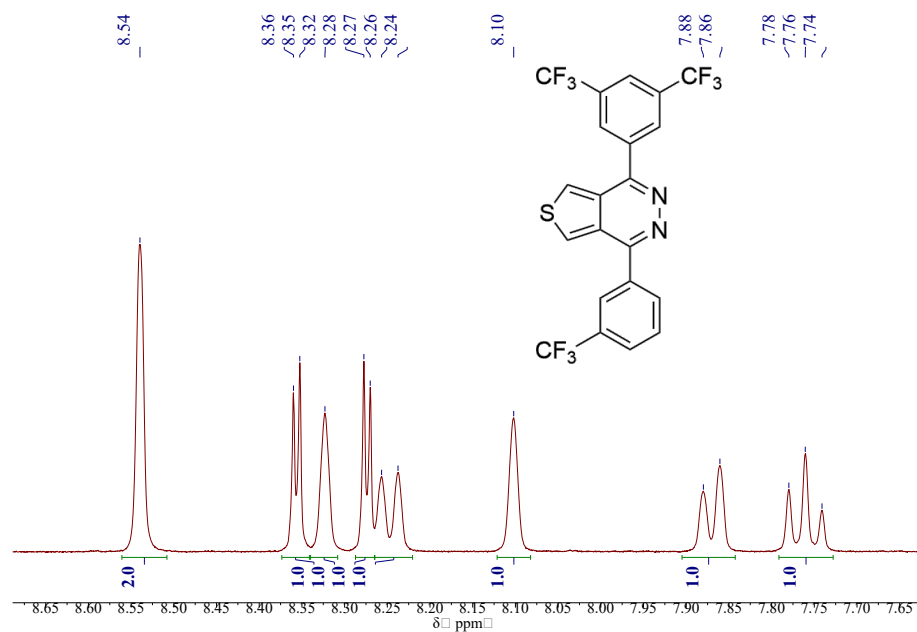
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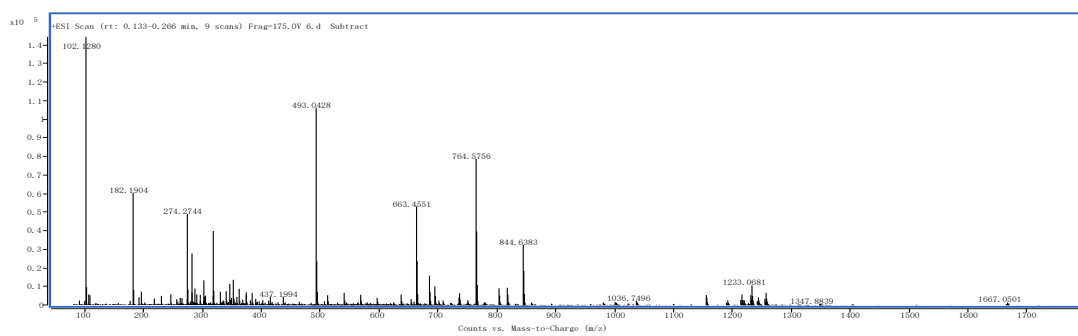
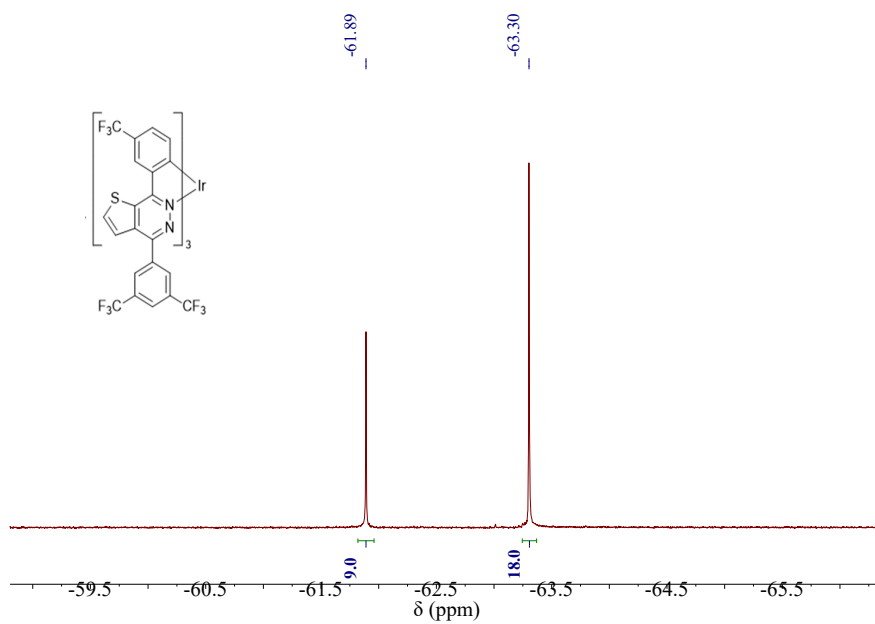
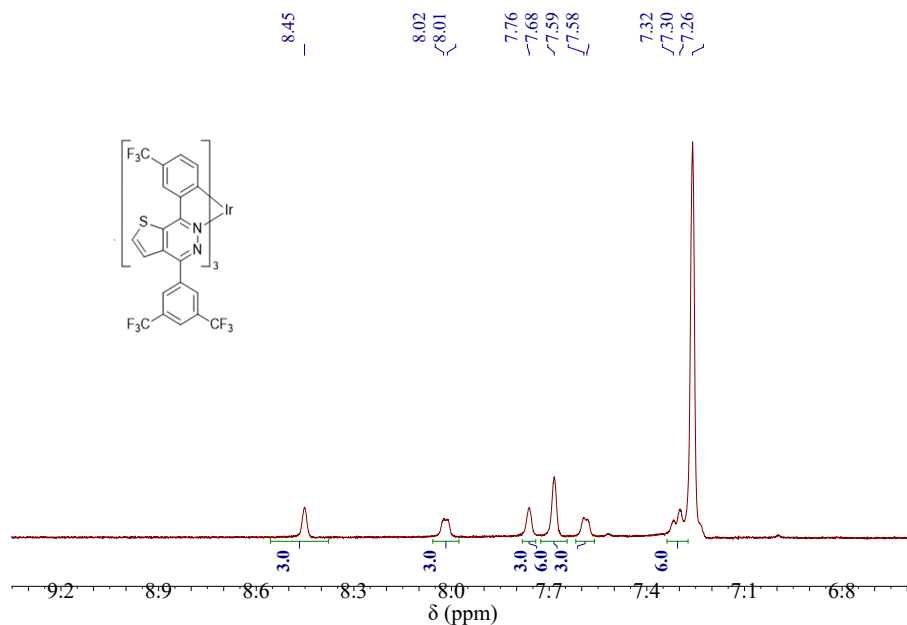
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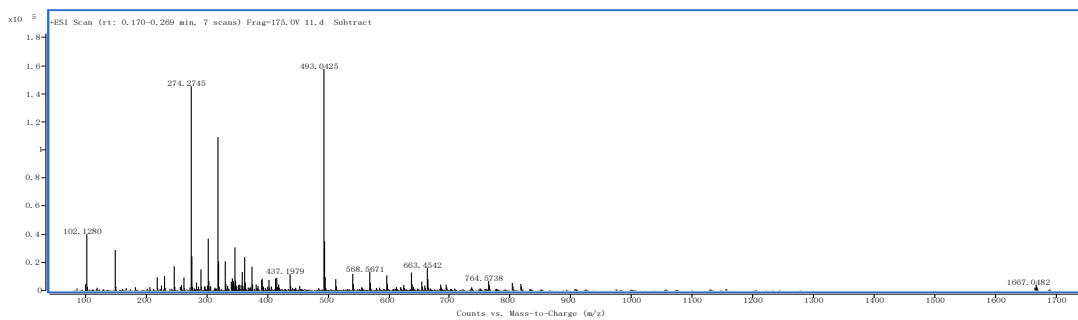
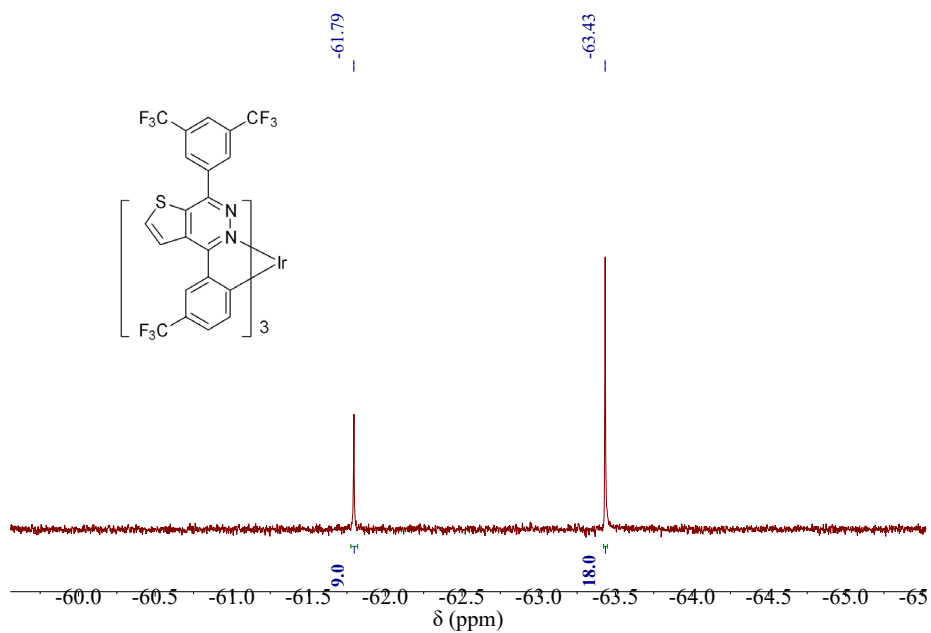
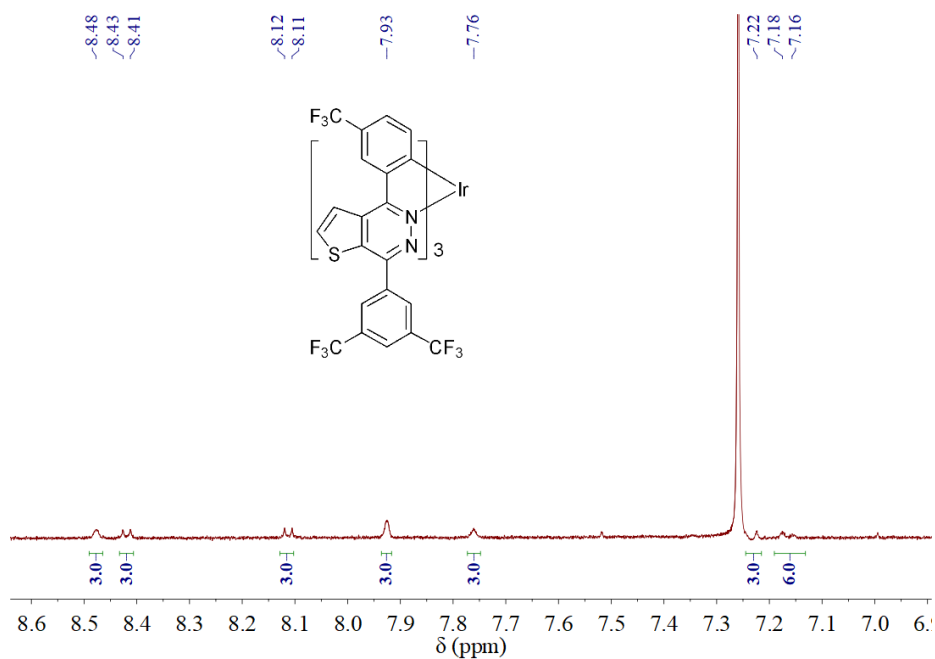
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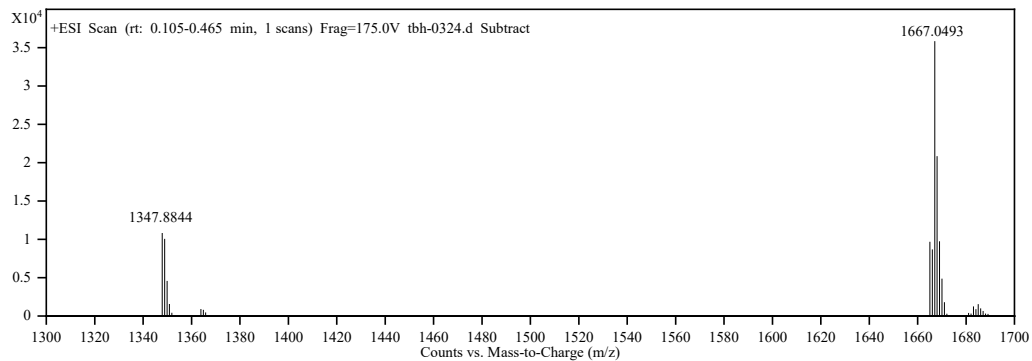
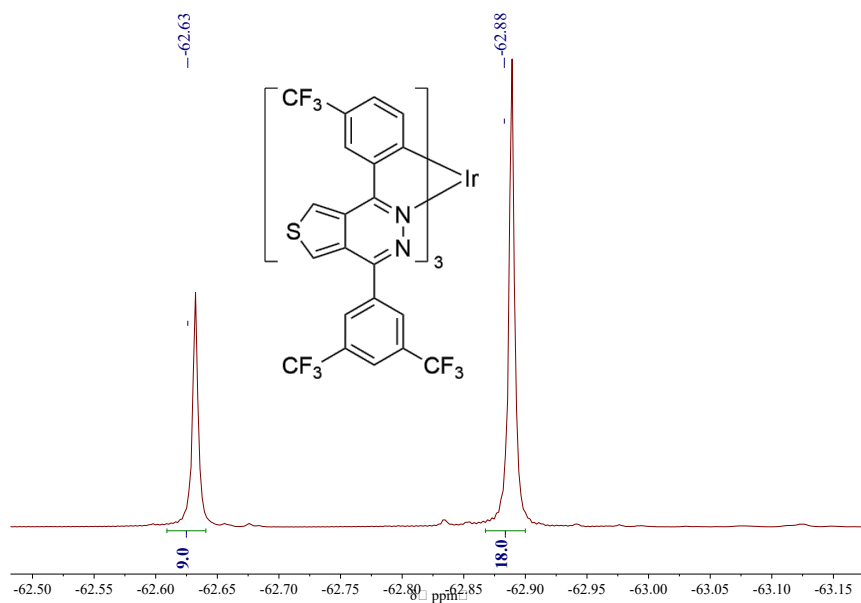
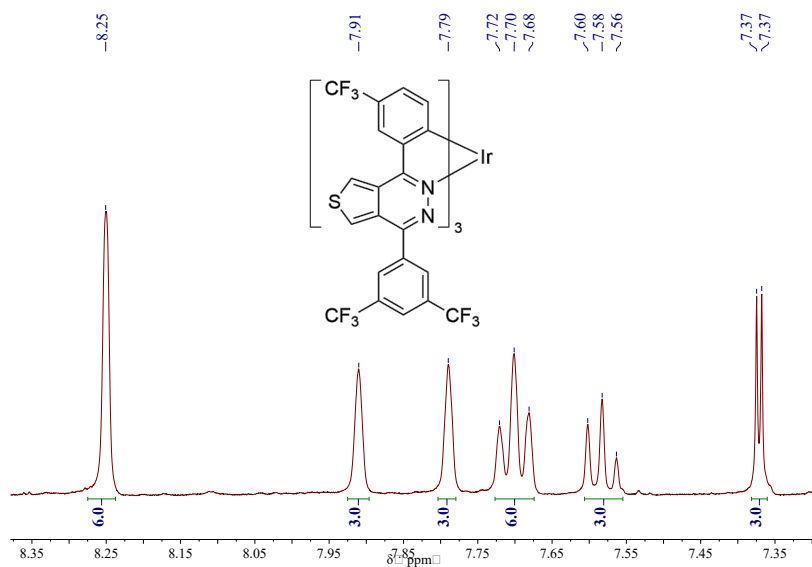
IrM:



IrP:



IrC:



4. The detailed crystallographic data of IrM.

Crystallographic and refinement data for complexes	
compound	IrM
Empirical formula	$C_{63}H_{24}F_{27}IrN_6S_3$
Formula weight	1666.21
Temperature	193.00 K
Wavelength	0.71073 Å
Crystal system	Trigonal
Space group	R -3
Unit cell dimensions	a = 17.0640(6) Å $\alpha = 90^\circ$ b = 17.0640(6) Å $\beta = 90^\circ$ c = 42.016(3) Å $\gamma = 120^\circ$.
Volume	10595.2(11) Å ³
Z	6
Density (calculated)	1.727 Mg/m ³
Absorption coefficient	2.247 mm ⁻¹
F(000)	5376
Theta range for data collection	2.379 to 27.471°.
Index ranges	-22 ≤ h ≤ 19, -21 ≤ k ≤ 22, -54 ≤ l ≤ 53
Reflections collected	52585
Independent reflections	5415 [R(int) = 0.0589]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6036

Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	5415 / 0 / 301
Goodness-of-fit on F ²	1.079
Final R indices [I > 2σ(I)]	R1 = 0.0408, wR2 = 0.1139
R indices (all data)	R1 = 0.0468, wR2 = 0.1189
Extinction coefficient	n/a
Largest diff. peak and hole	1.309 and -0.750 e.Å ⁻³

5. 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.