

Supporting Information

Synthesis of 5-Fluoro-dihydroindolizines from Pyrrole-2-Acetic Acids and Trifluoromethyl Alkenes via Dual C-F Bond Cleavage in a CF₃ Group

Zhengchang Sun and Lei Zhou*

School of Chemistry, Sun Yat-Sen University, Guangzhou, 510006, China.

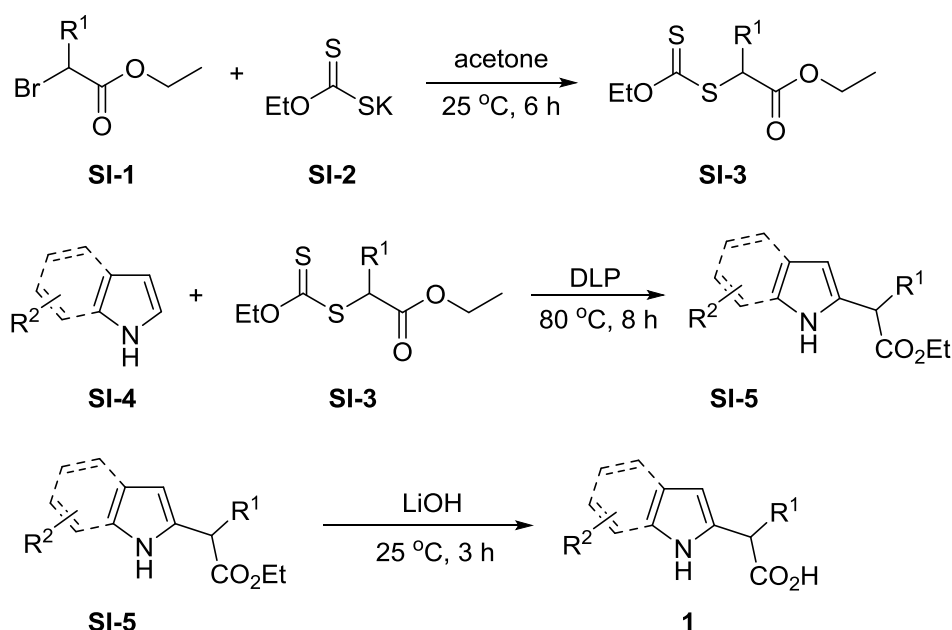
E-mail: zhoul39@mail.sysu.edu.cn

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1. General procedures for the synthesis of pyrrole-2-acetic acids and indole-2-acetic acids 1

All the pyrrole-2-acetic acids and indole-2-acetic acids are commercially available reagents, but are very expensive. Therefore, they were prepared from the corresponding pyrroles and indoles *via* radical alkylation followed by hydrolysis according to the modified procedure of Zard (Huang, Q.; Zard, S. Z. *Org. Lett.* **2018**, *20*, 1413–1416).



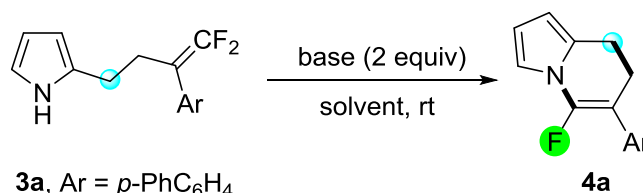
Synthesis of Xantate SI-3: To a 250 mL round flask was added α -bromo acetate **SI-1** (20 mmol) and acetone (100 mL). Then the potassium ethyl xanthogenate **SI-2** (4 g, 25 mmol) was added in portions at 0 °C, then the solution was allowed to stir at room temperature for 6 h. After completion of the reaction, the reaction mixture was evaporated under reduced pressure, then dissolved with water (75 mL) and extracted with dichloromethane (3×75 mL). The organic layer was washed with brine, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure to give Xantate **SI-3** as yellow oil, which can be used for the next step of reaction without further purification.

Radical alkylation of pyrroles or indoles using Xantate SI-3: A solution of **SI-4** (10 mmol) and Xantate **SI-3** (12.5 mmol) in a 1,2-dichloroethane (20 mL) was refluxed in

a heating mantle under nitrogen for 10 min. The dilauroyl peroxide (DLP, 4.98 g, 12.5 mmol) was dissolved in 1,2-dichloroethane (30 mL) and added by dropwise for a period of 5 h. After addition, the solution was stirred for additional 2 h. Then the reaction mixture was cooled down to room temperature, concentrated under reduced pressure and purified by flash chromatography (petroleum ether: ethyl acetate = 25:1) on silica gel to provide esters **SI-5**.

Hydrolysis of esters **SI-5**: LiOH (240 mg, 10 mmol) dissolved in water (15 mL) was added to the THF (15 mL) solution of ester **SI-5** (5 mmol) in a 50 mL round bottom flask. The mixture stirred rapidly at room temperature for 3 h. Upon completion of the reaction, as monitored by TLC, the solution was neutralized with HCl (1 mol/L) to PH = 2 and extracted with Et₂O (3x40ml). The organic layer was dried over anhydrous Na₂SO₄ and evaporated under reduced pressure to afford the corresponding pure acids as white solid, which can be used directly without further purification.

2. Table S1. Optimization conditions for intramolecular S_NV reaction of **3a**^a



entry	base	solvent	time (h)	Yield (%) ^b
1	NaOH	DMSO	4	67
2	K ₃ PO ₄	DMF	12	0
3	Na ₂ CO ₃	DMF	12	0
4	<i>t</i> BuOLi	DMF	4	34
5	DBU	DMF	4	<5
6	NaH	DMF	1	60
7	NaOH	DMF	1	89

^a Reaction conditions: **3a** (0.2 mmol), base (2 equiv), solvent (1.5 mL), rt. ^b Isolated yields.

3. Cyclic voltammetry measurement

Cyclic voltammogram was recorded on a CHI750E Electrochemical Analyzer using a three-electrode cell at room temperature. Electrochemical potentials were obtained with a standard set of conditions to main internal consistency. Cyclic voltammograms were collected with a potentiostat. A glassy carbon electrode was used as the working electrode and a platinum wire as the auxiliary electrode. The reference electrode was a saturated Ag/AgCl electrode. Lithium perchlorate was used as the supporting electrolyte. Samples were prepared by dissolving 1 mmol of **1a**, 2 mmol of DABCO and LiClO₄ (1 mmol) in 5 mL of anhydrous DMSO and purged with nitrogen.

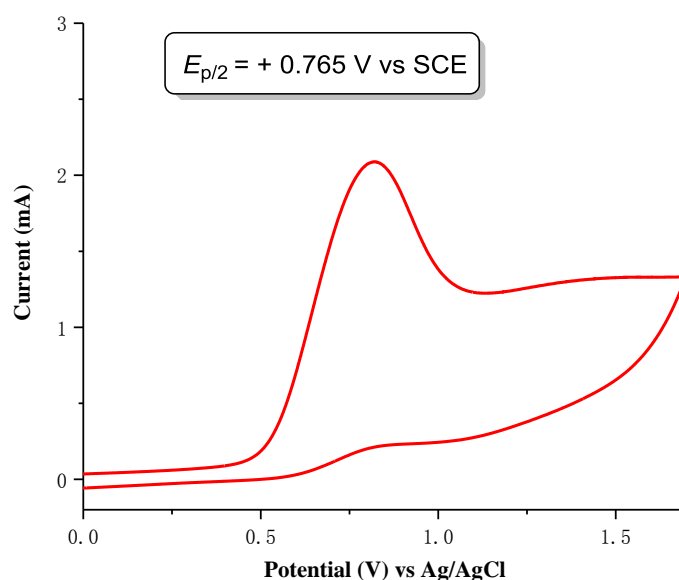
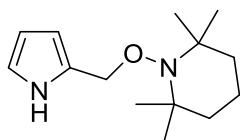


Figure S1. Cyclic voltammogram of pyrrole-2-acetic acid **1a** in the presence of DABCO in DMSO.

As shown in Figure S1, in the presence of base, the carboxylate form of **1a** showed an irreversible oxidation peak at +0.808 V. The value for $E_{p/2}$ was referenced to SCE (Saturated Calomel Electrode) by reducing 0.043 V to the measured potential.

4. HRMS spectrum of pyrrole-2-methyl-TMEPO adduct



HRMS (ESI) Calcd for $C_{14}H_{25}N_2O$ $[M+H]^+$ 237.1961, found: 237.1958.

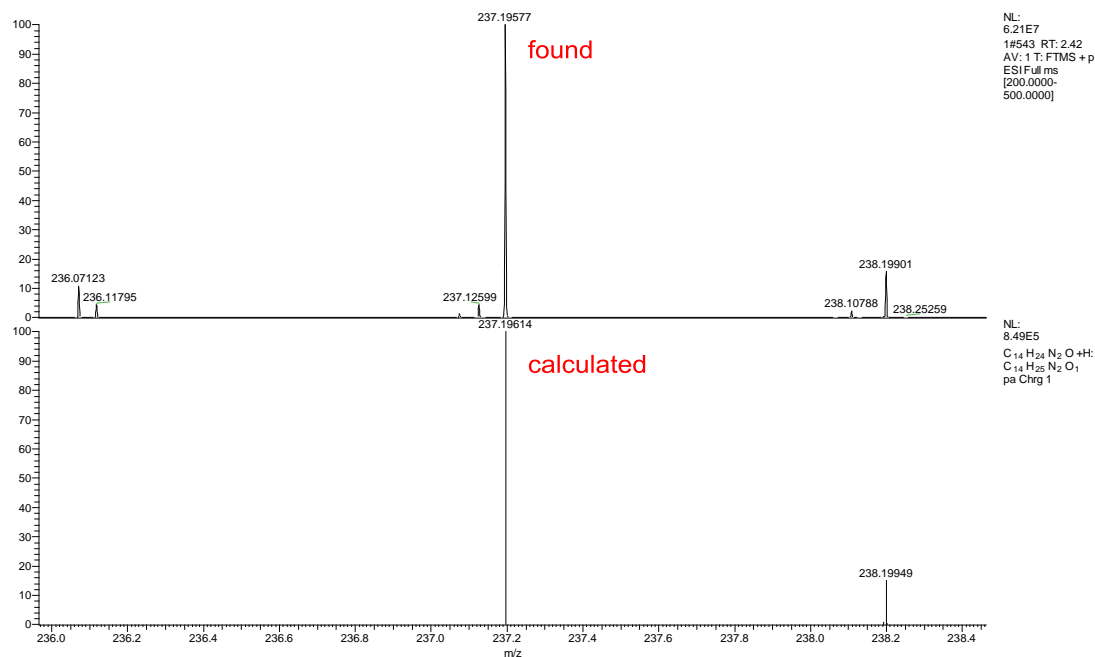


Figure S2. HRMS spectrum of pyrrole-2-methyl-TMEPO adduct.

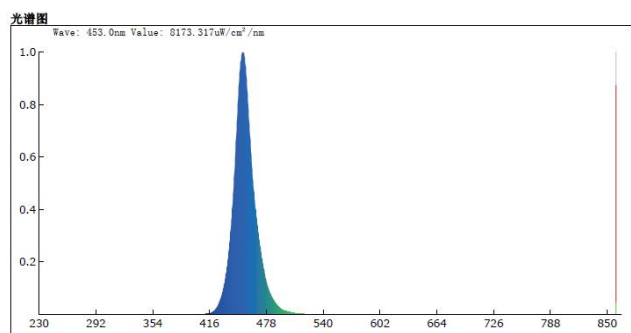
5. Light source and apparatus

The reactions were performed using RLH-18 8-position Photo Reaction System, which manufactured by Beijing Rogertech Co. Ltd based in Beijing, China (<http://www.rogertech.cn/>). This Photo reactor are equipped with eight 10 W blue light LEDs, and their power can be tuned by connecting a controller.

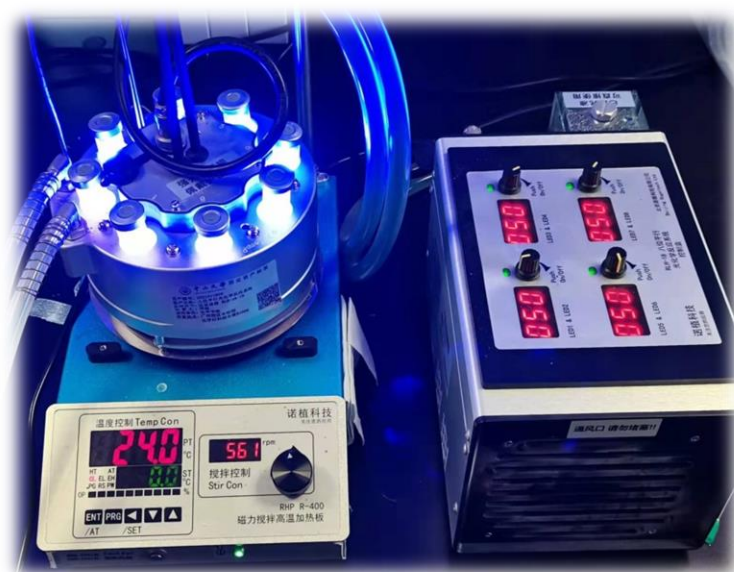
The emission spectrum of blue LEDs is about 416 to 510 nm, and its λ_{\max} is 453.6 nm. The strength of irradiation @5 W is about 246 mW/cm².

Irradiation vessel is borosilicate glass test tube. The reaction was irradiated through a high-reflection channel from blue LED to the test tube, which length is 2 cm without any filters.

The emission spectrum of the light source and the picture of the apparatus are shown below:

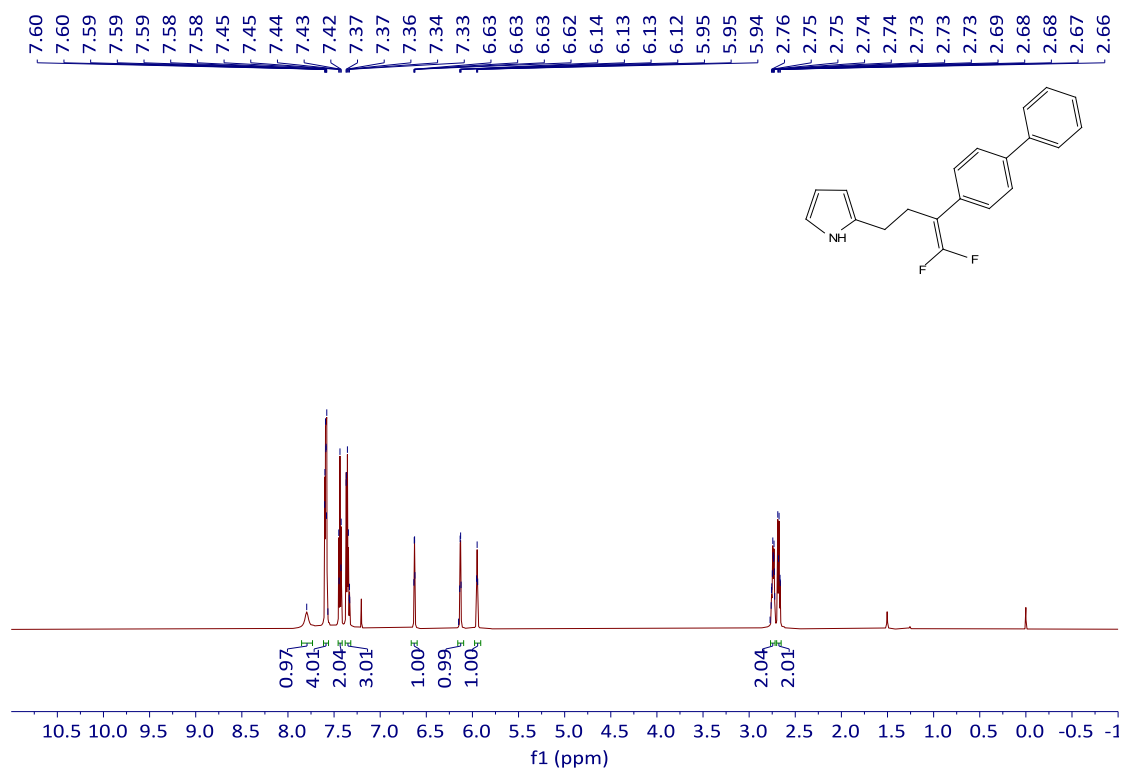


Scheme S1. The emission spectrum of the light source

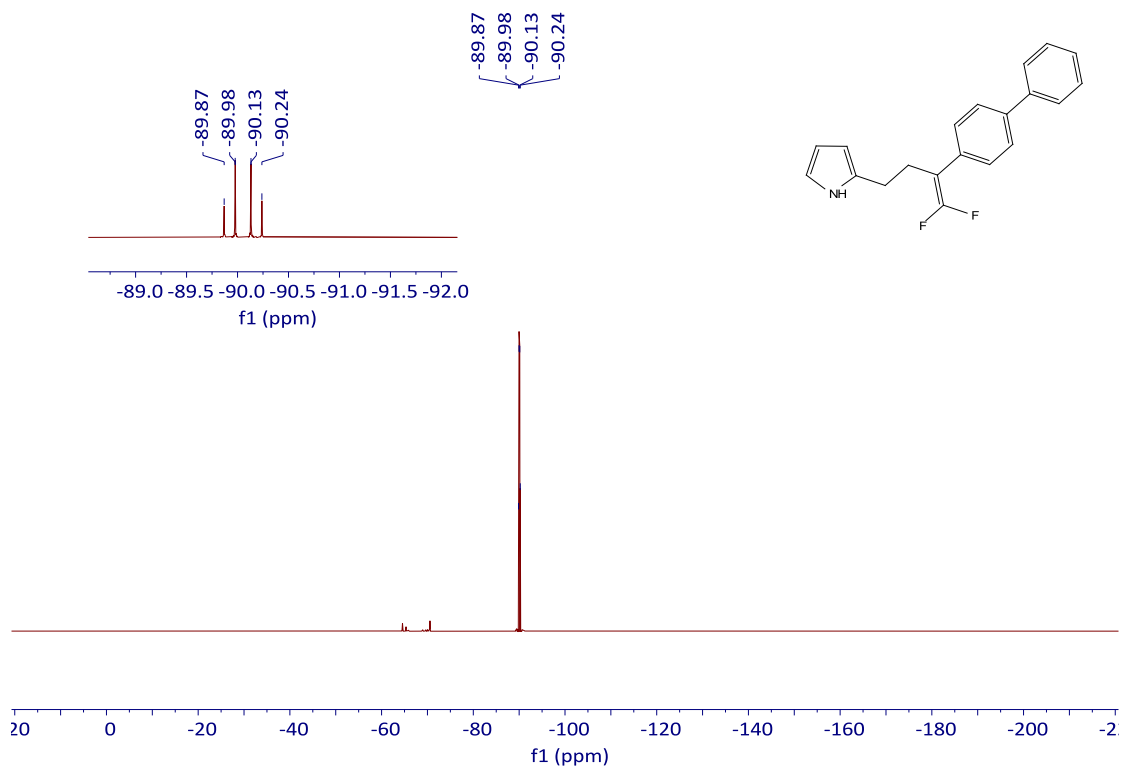


Scheme S2. The picture of apparatus.

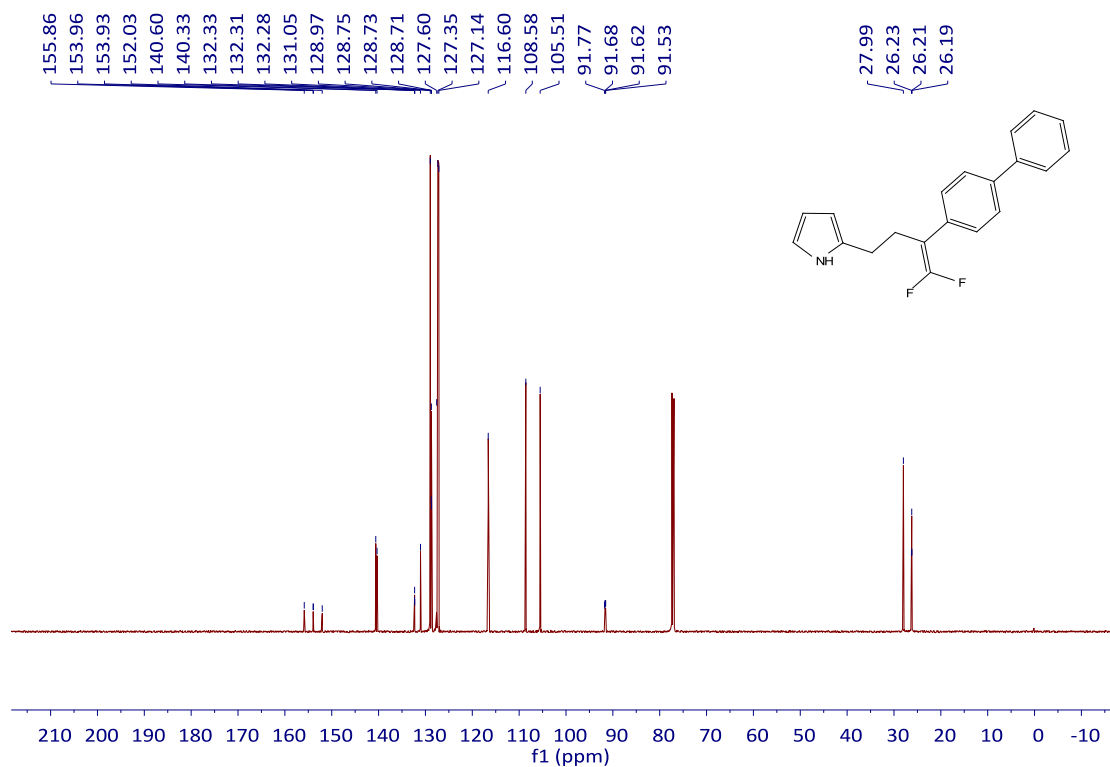
6. Copies of ^1H , ^{19}F , $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of products



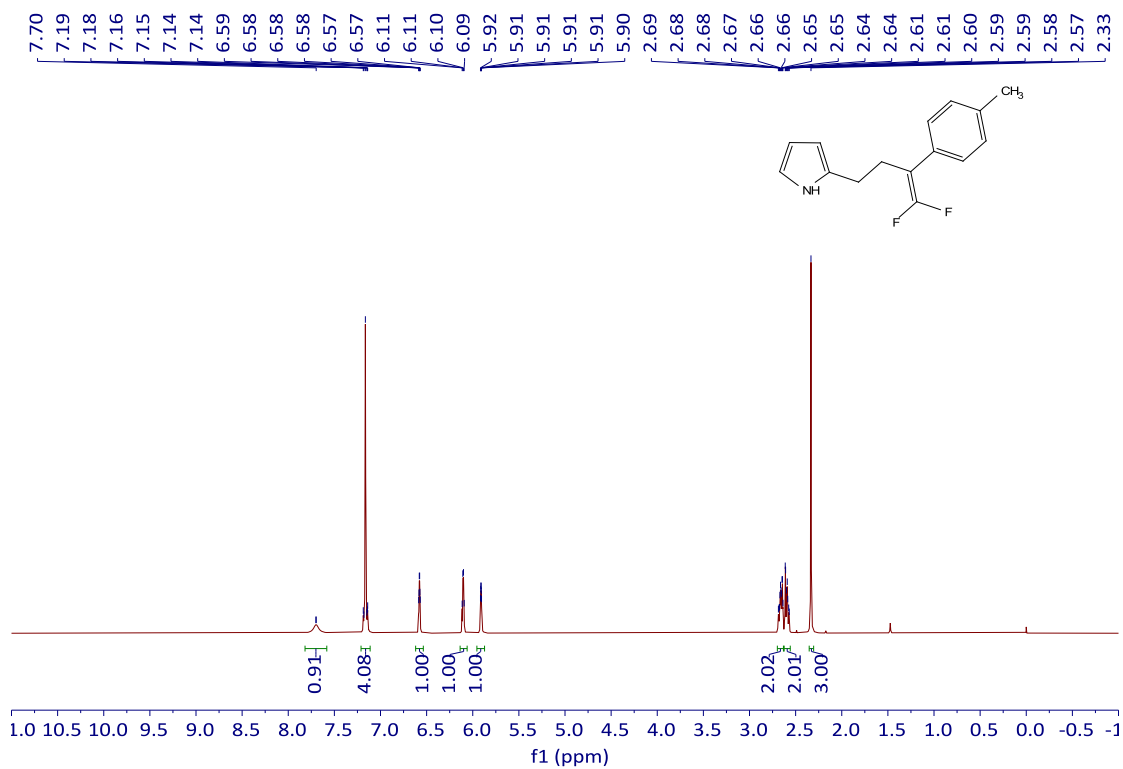
^1H NMR of **3a** (400 Hz, CDCl_3)



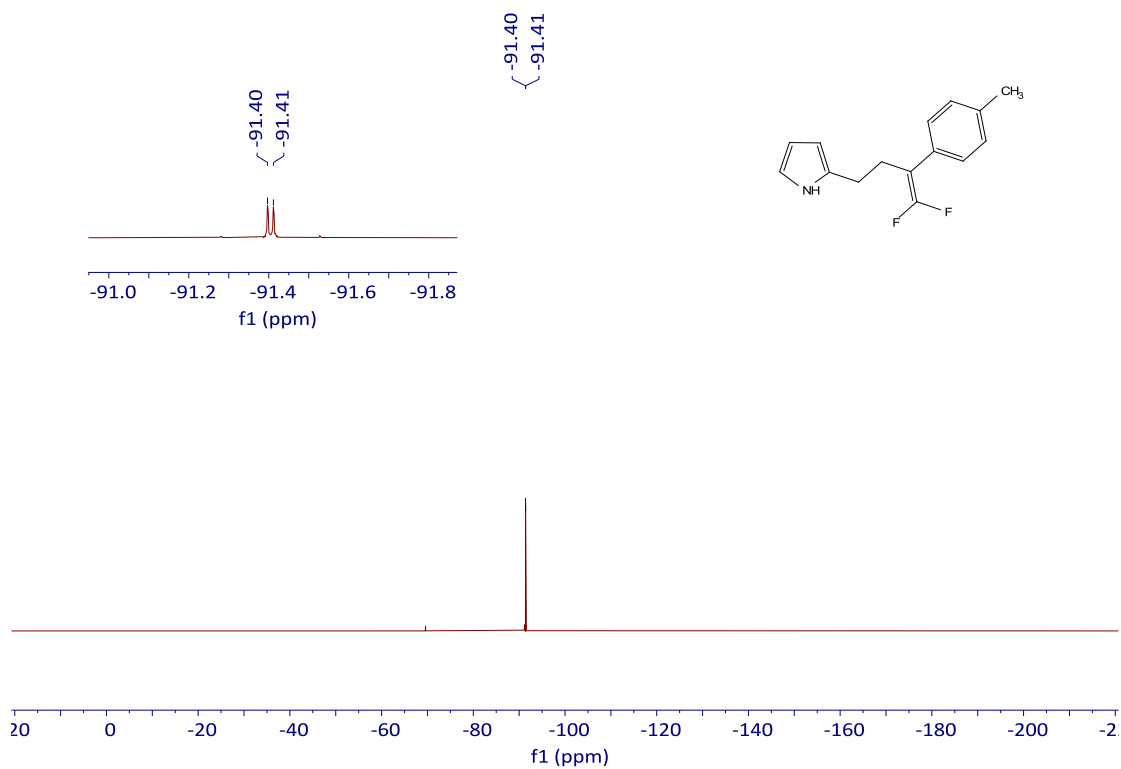
^{19}F NMR of **3a** (376 Hz, CDCl_3)



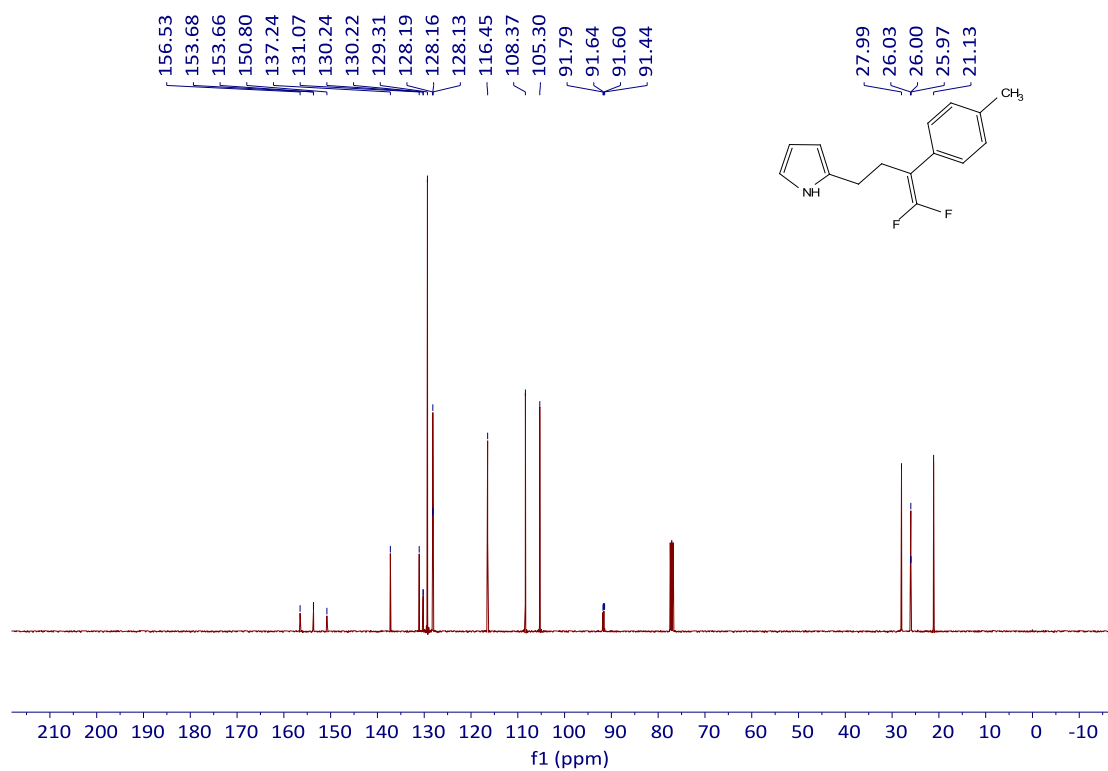
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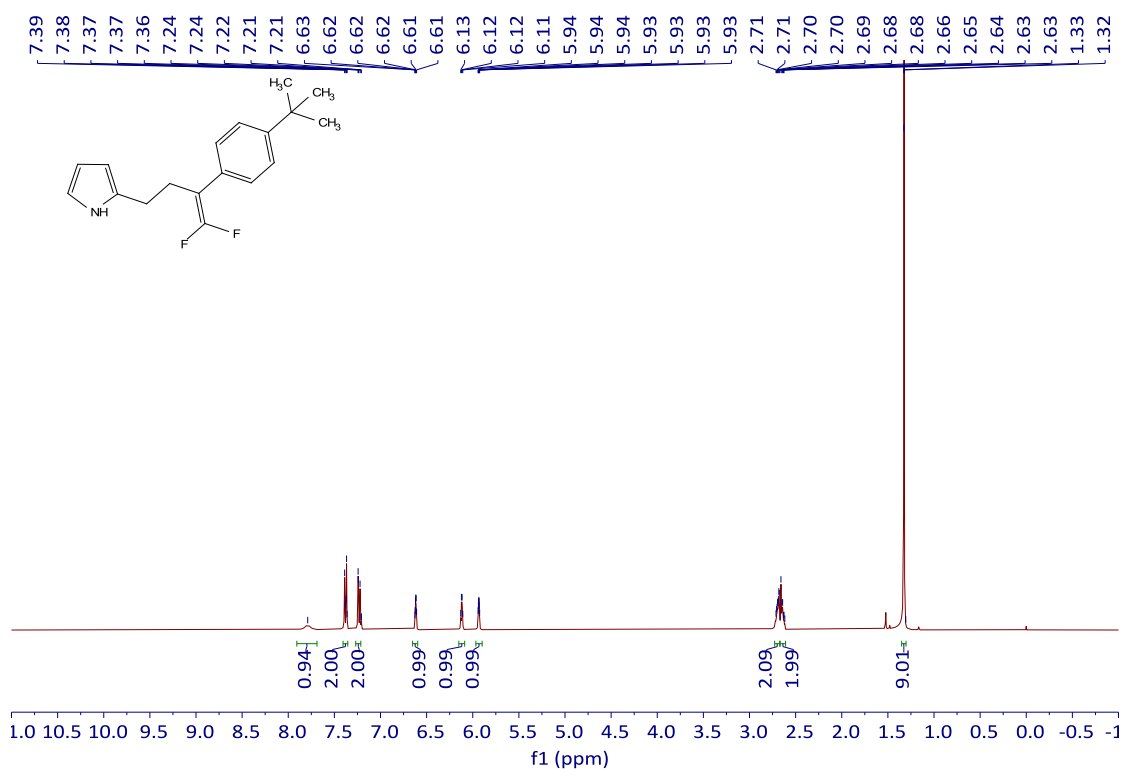
^1H NMR of **3b** (400 Hz, CDCl_3)



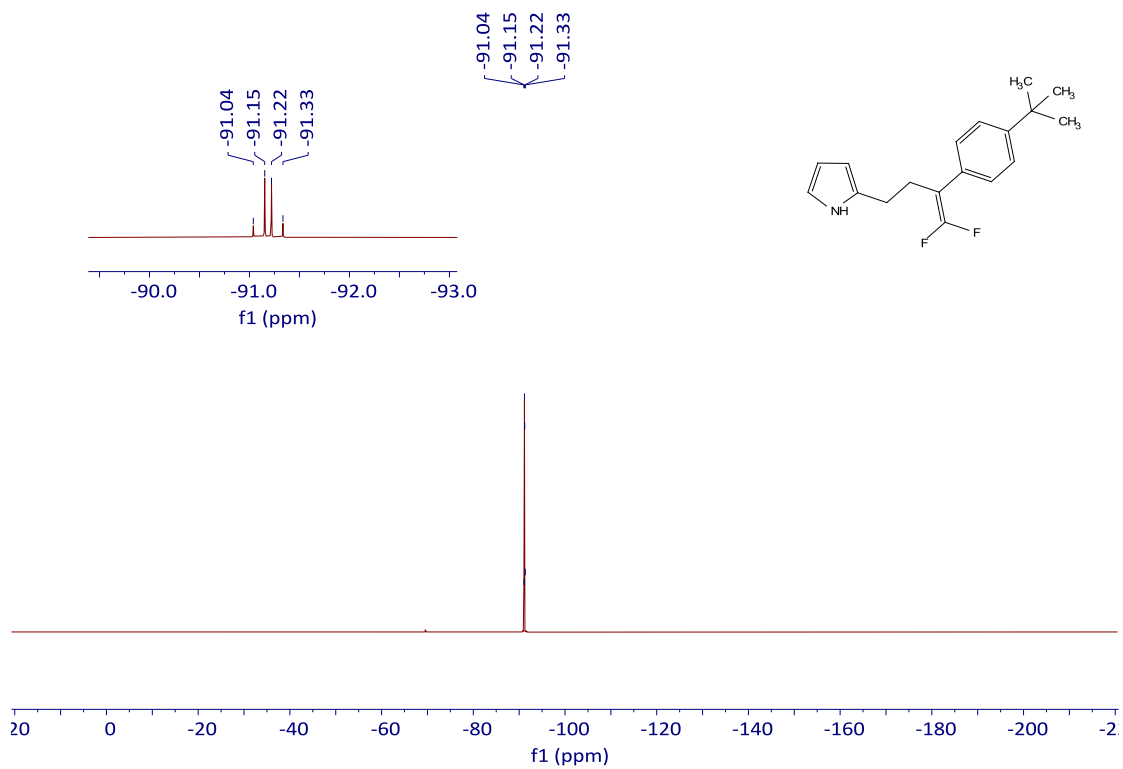
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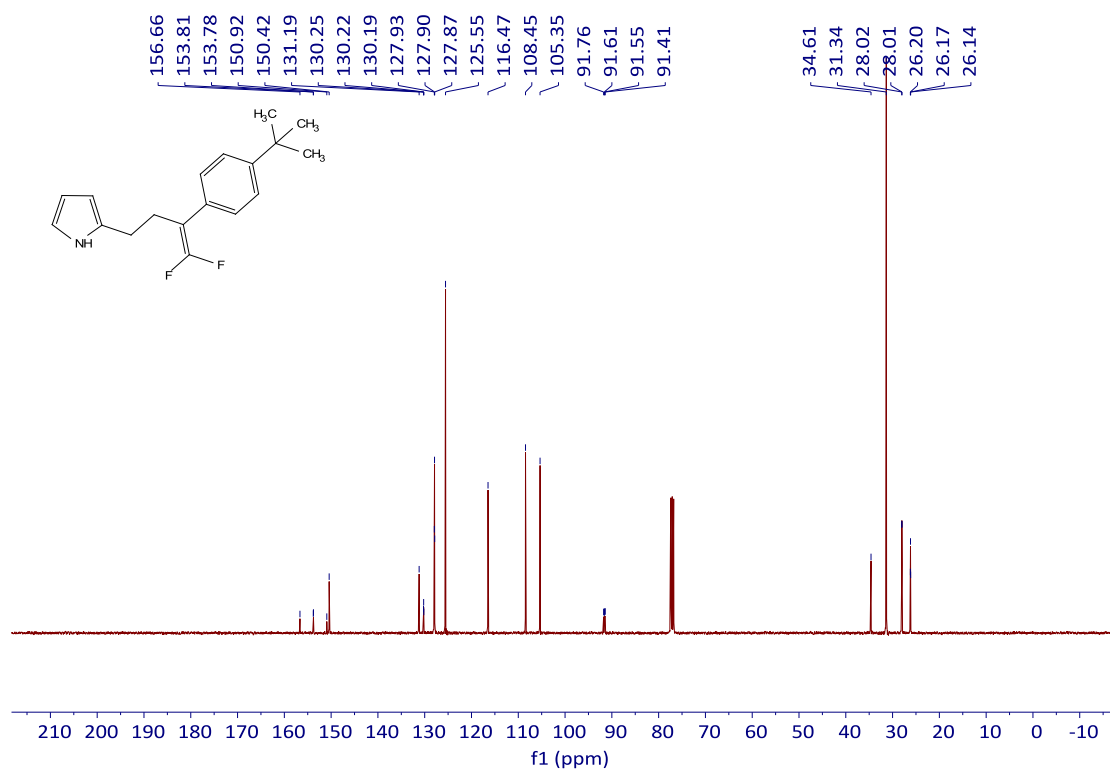
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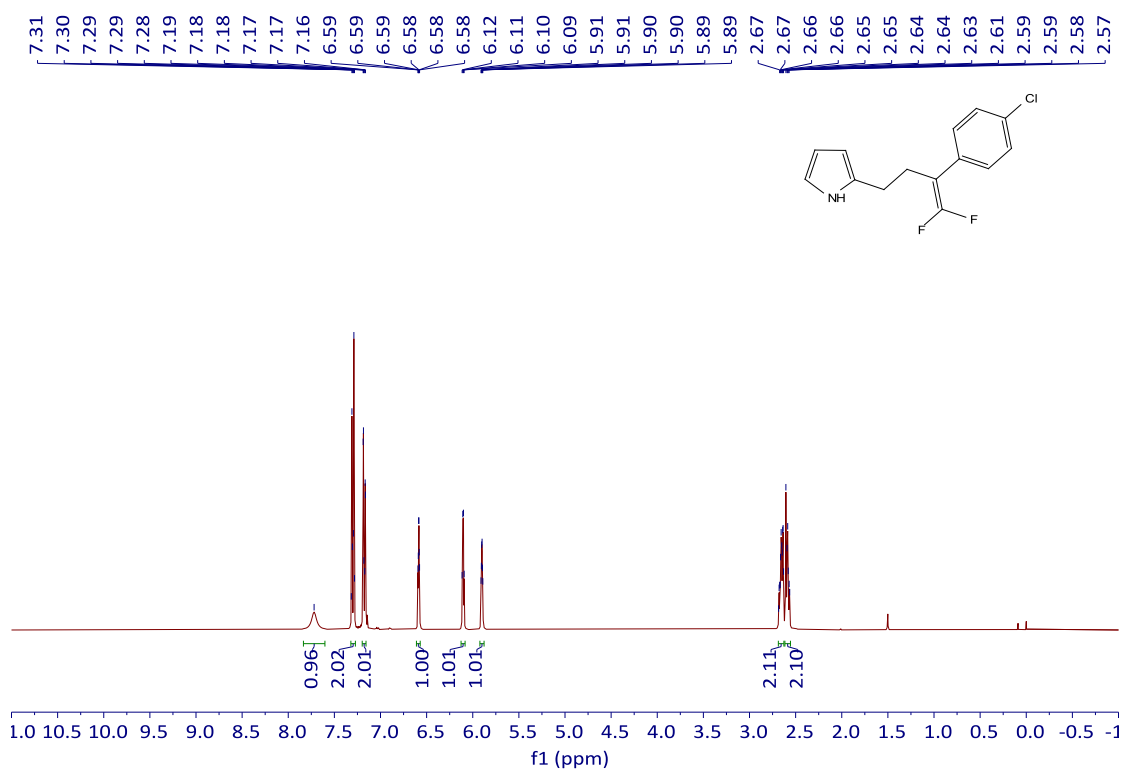
¹H NMR of **3c** (400 Hz, CDCl₃)



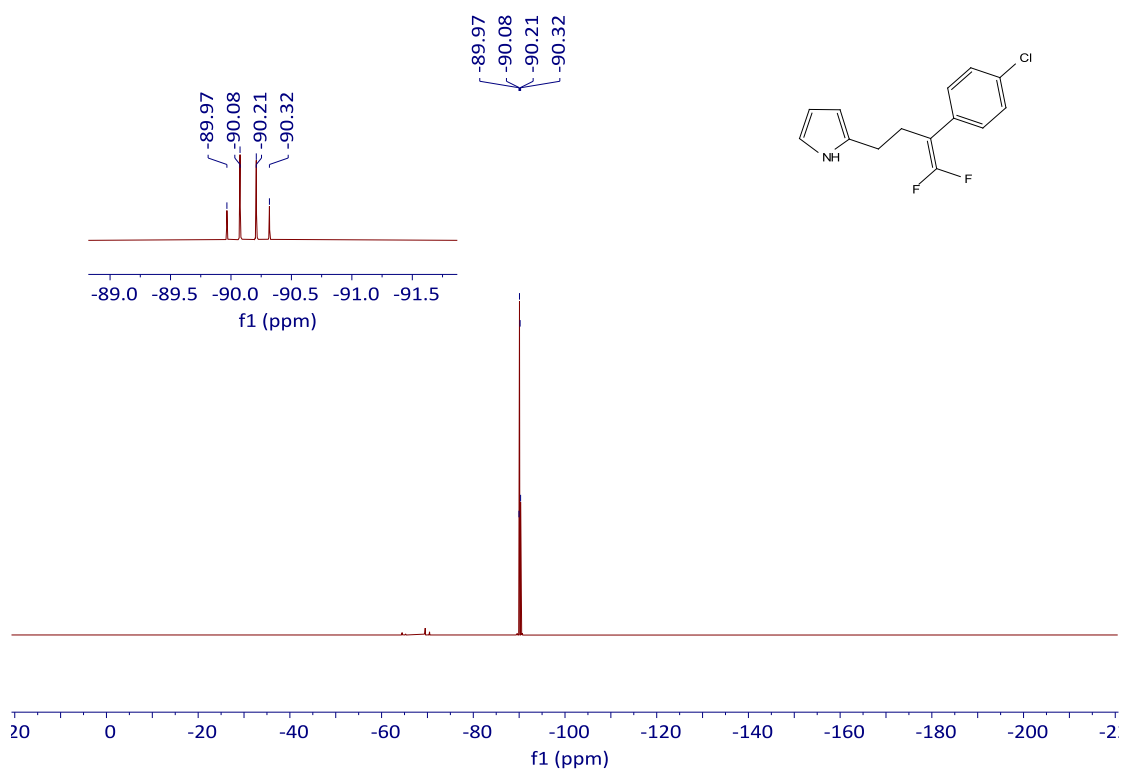
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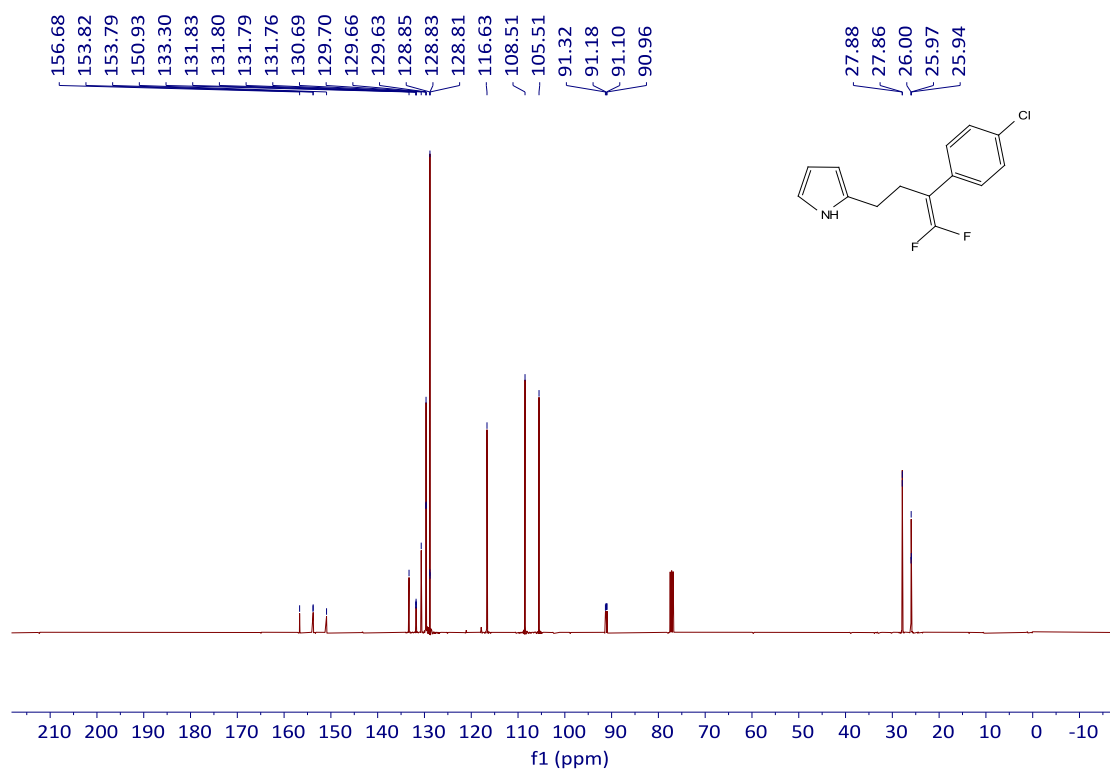
¹³C{¹H} NMR of **3c** (100 Hz, CDCl₃)



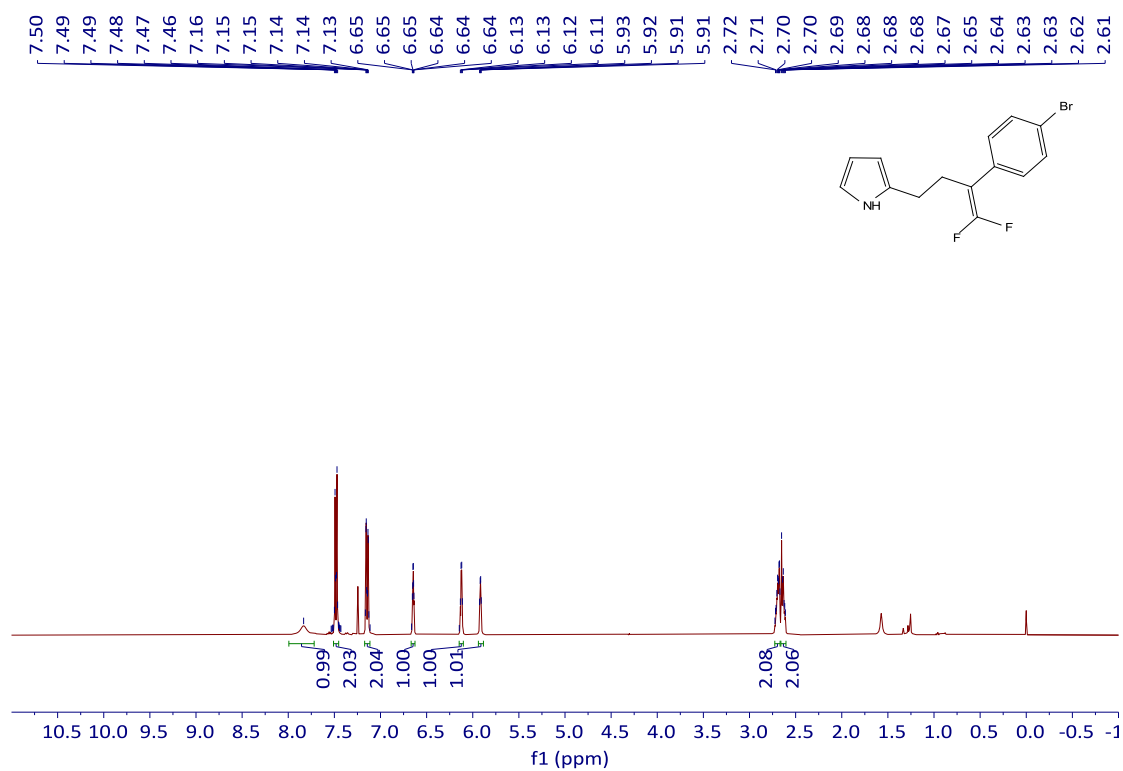
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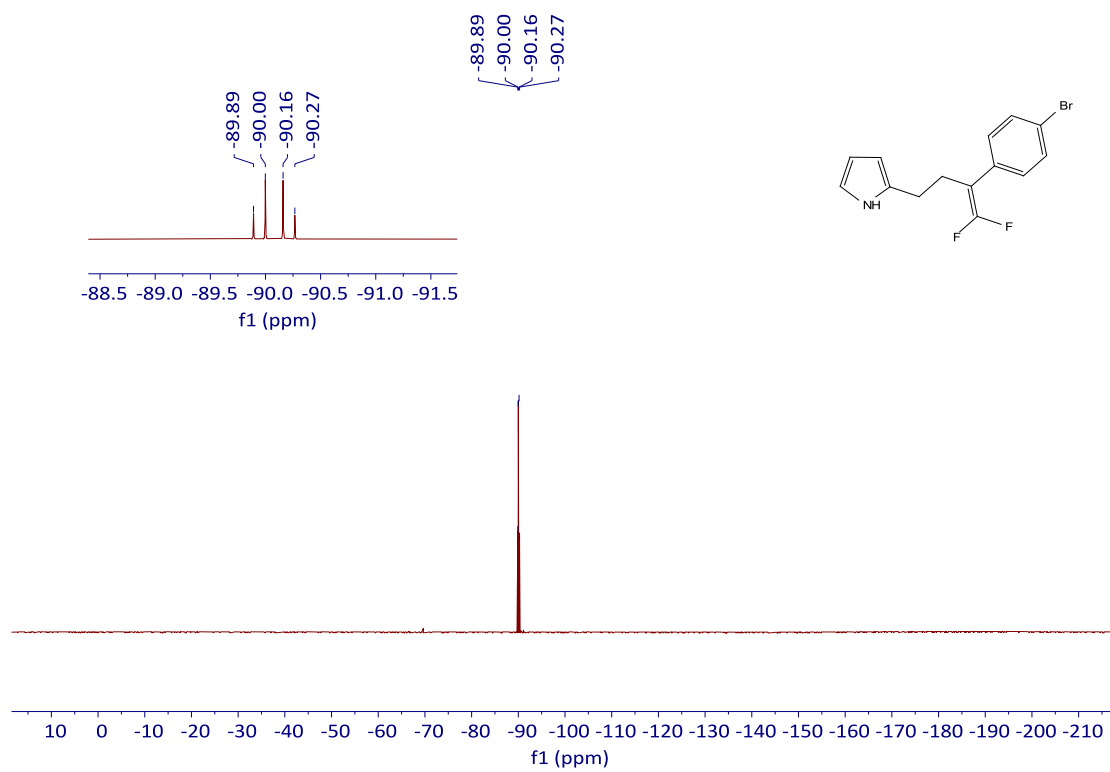
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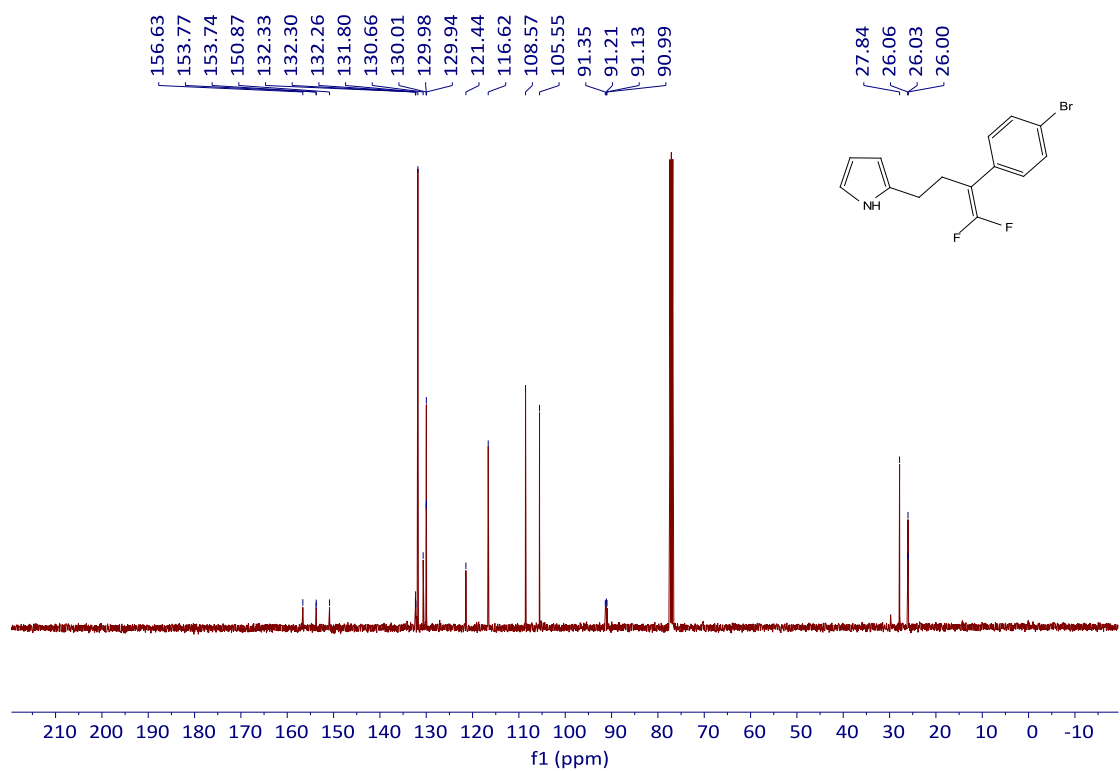
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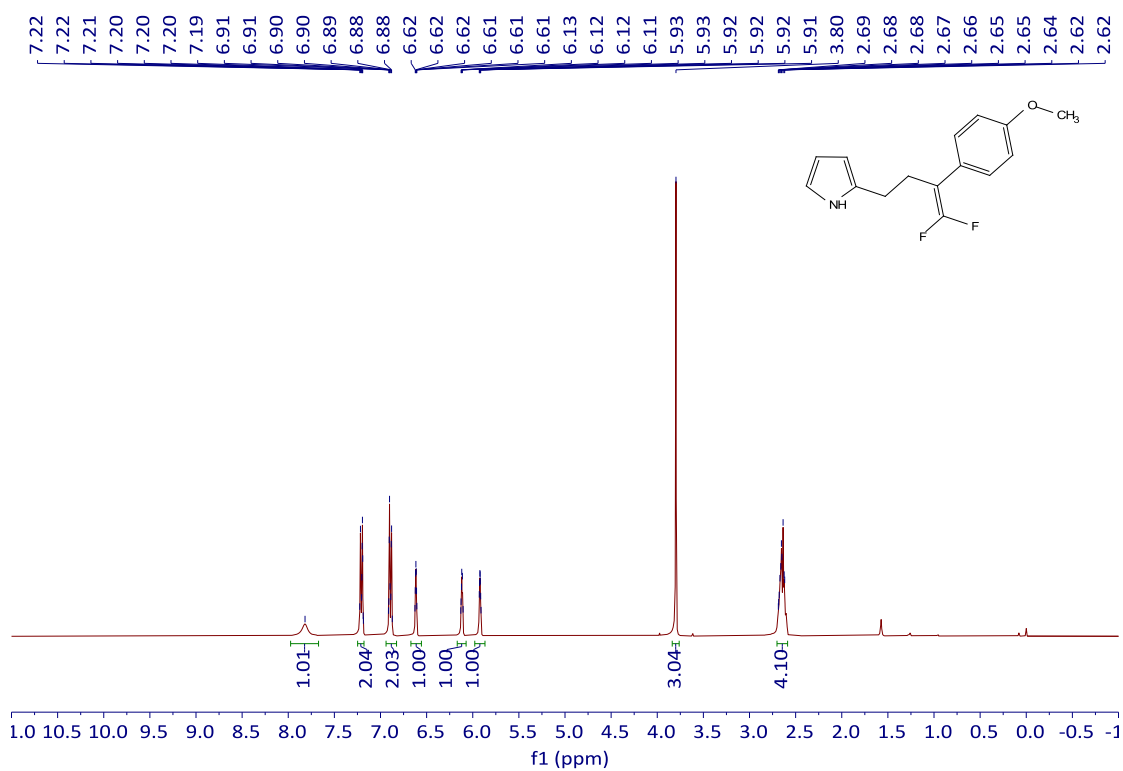
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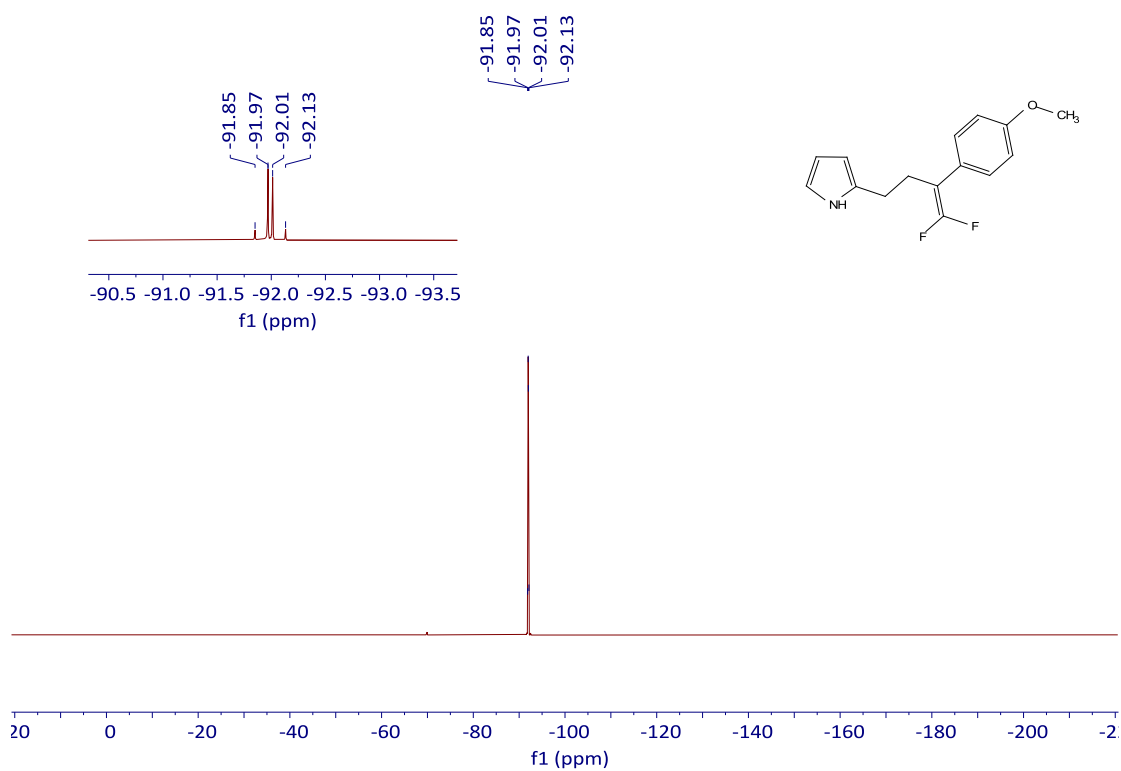
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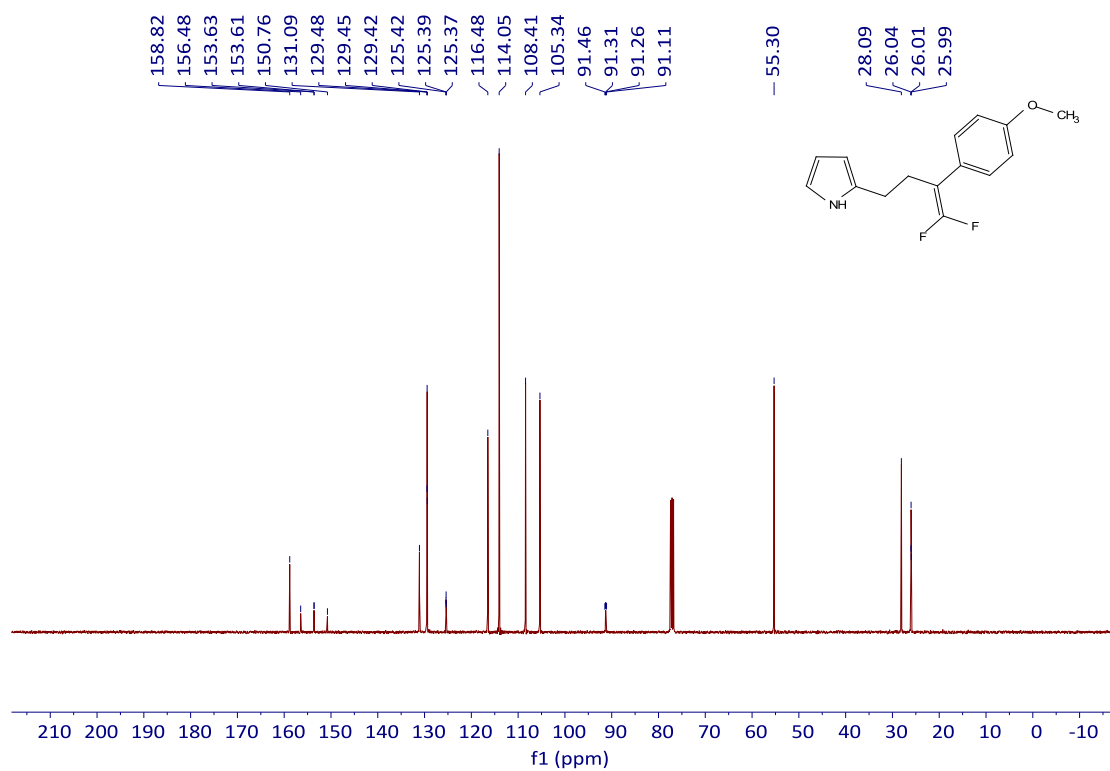
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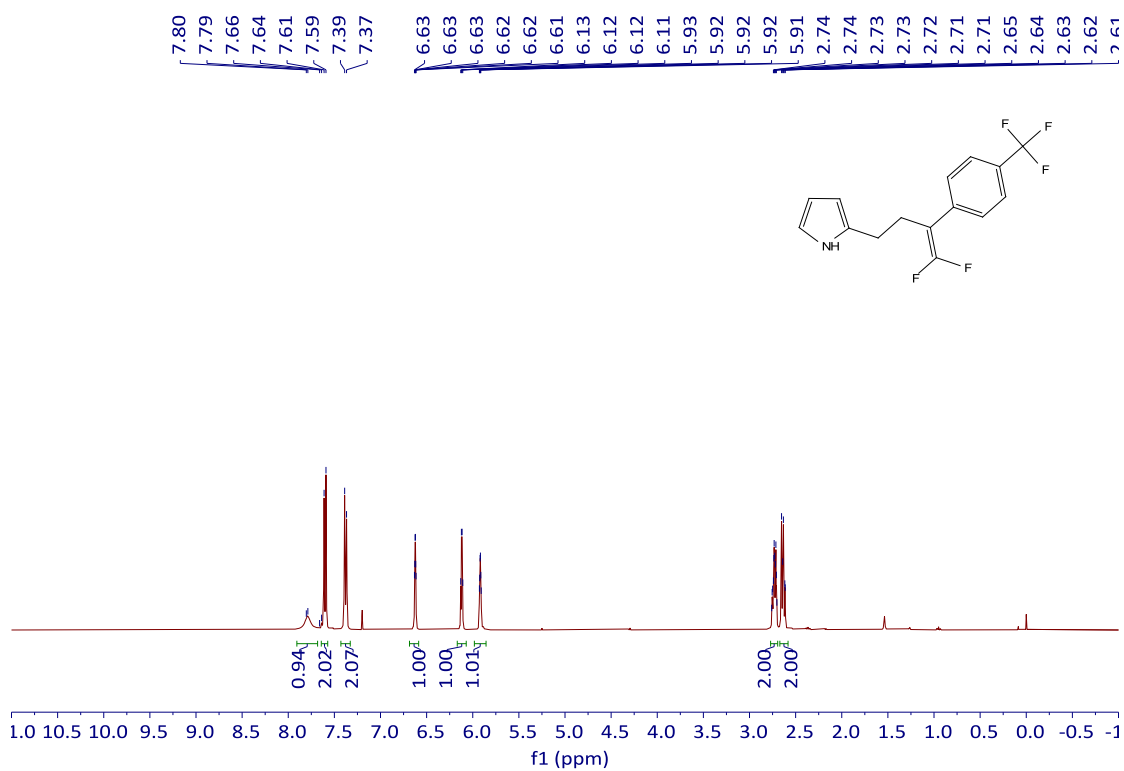
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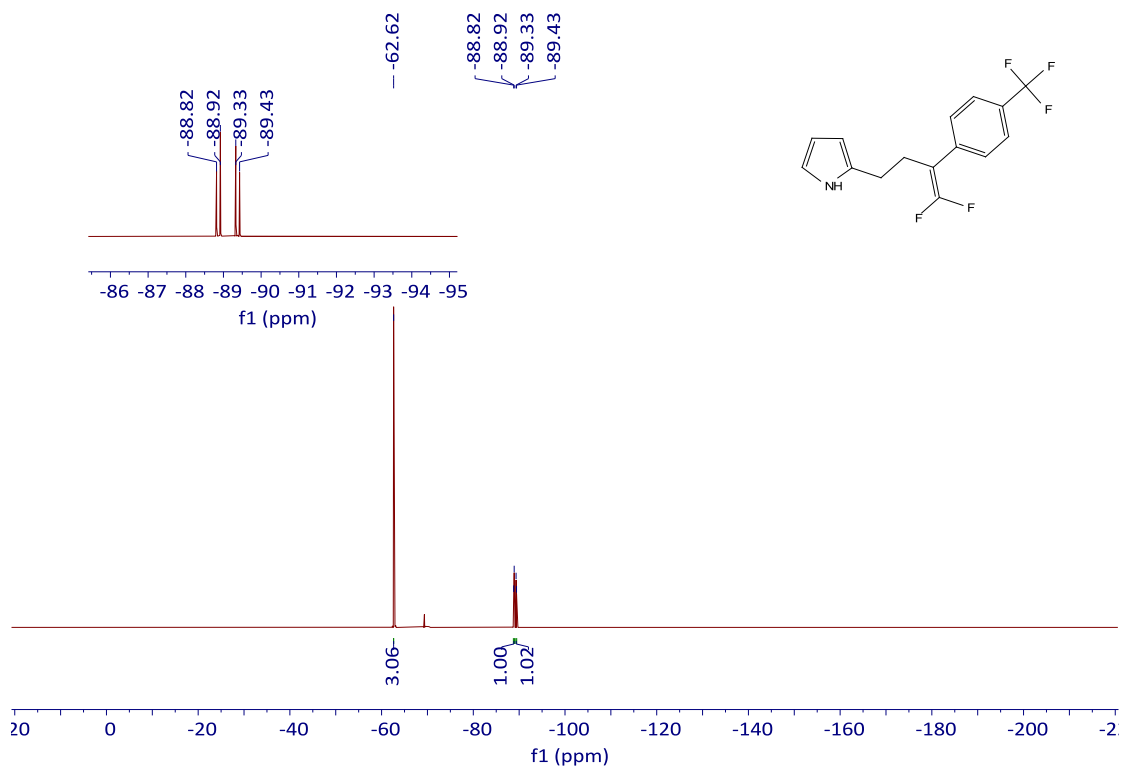
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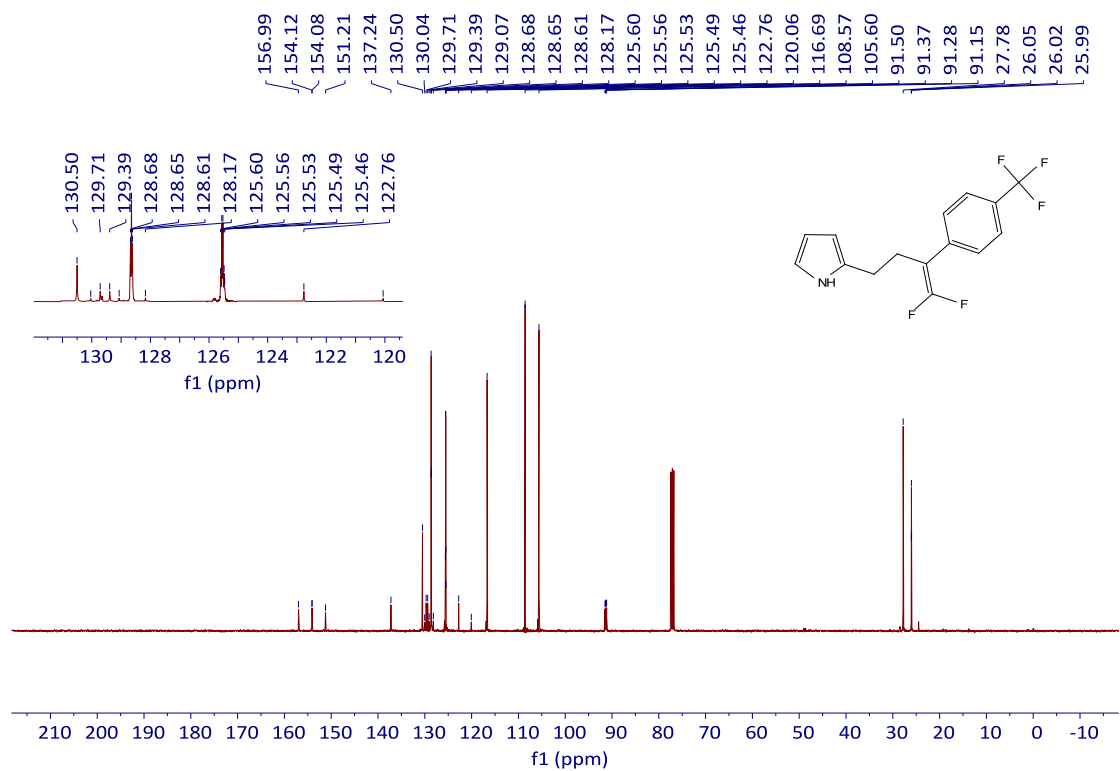
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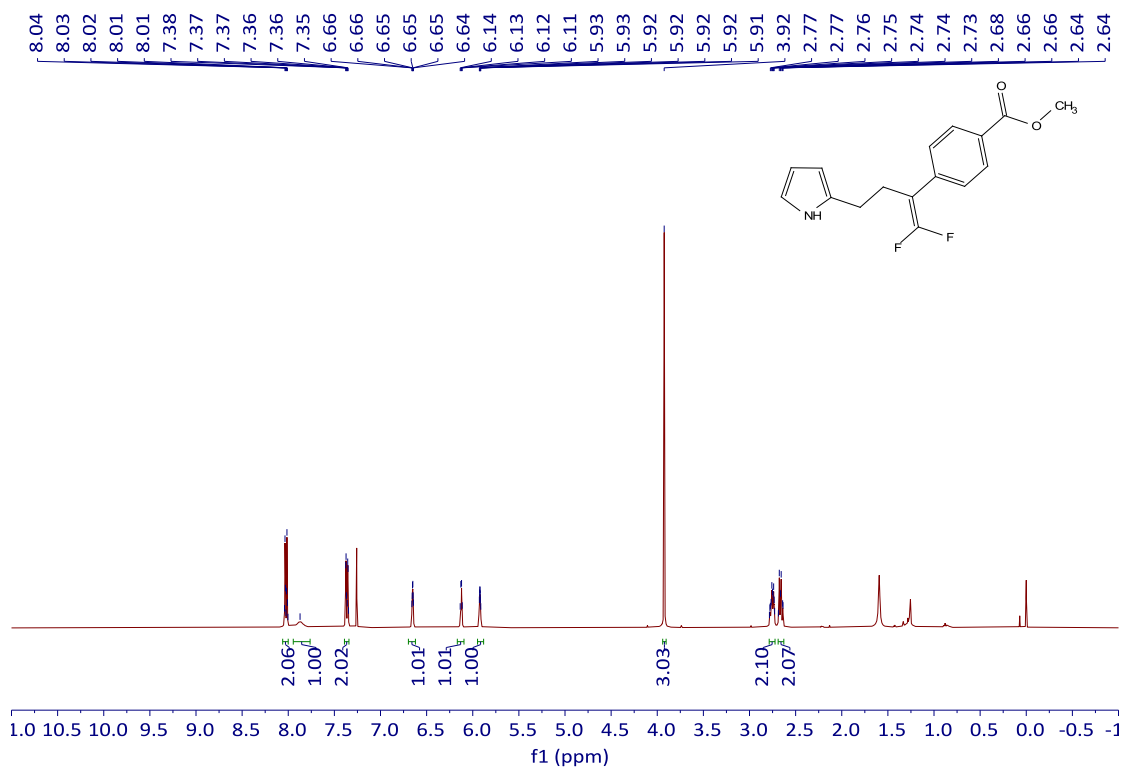
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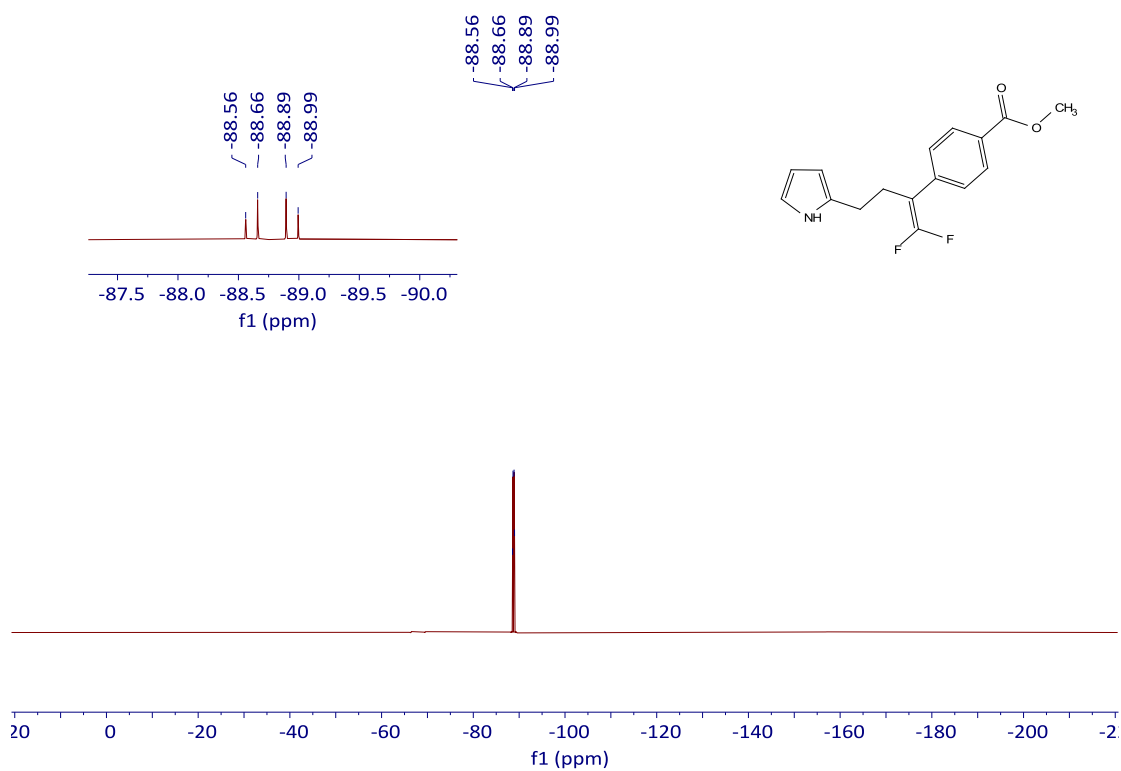
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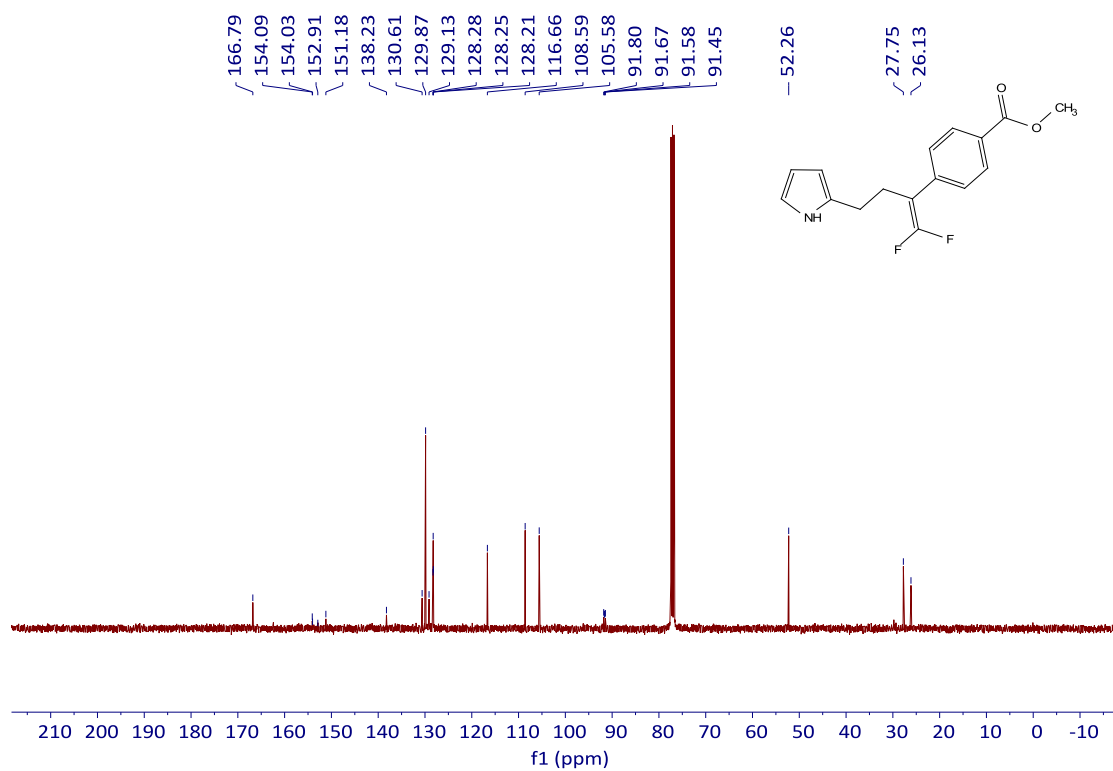
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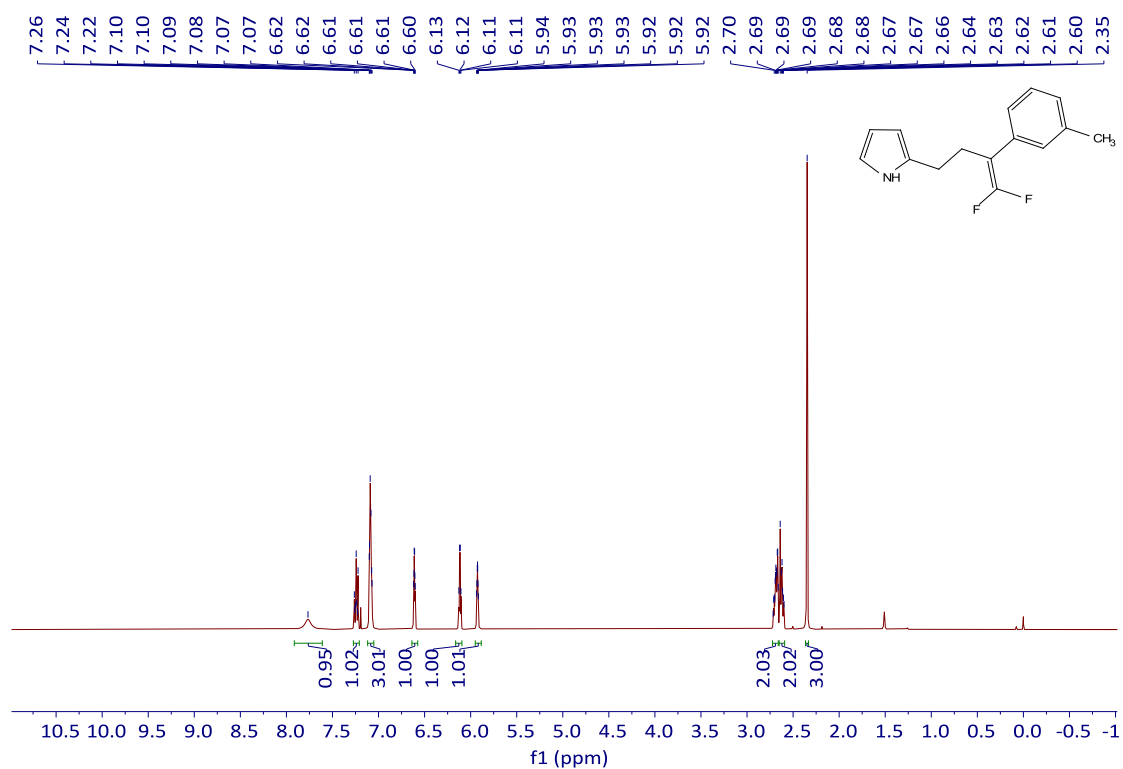
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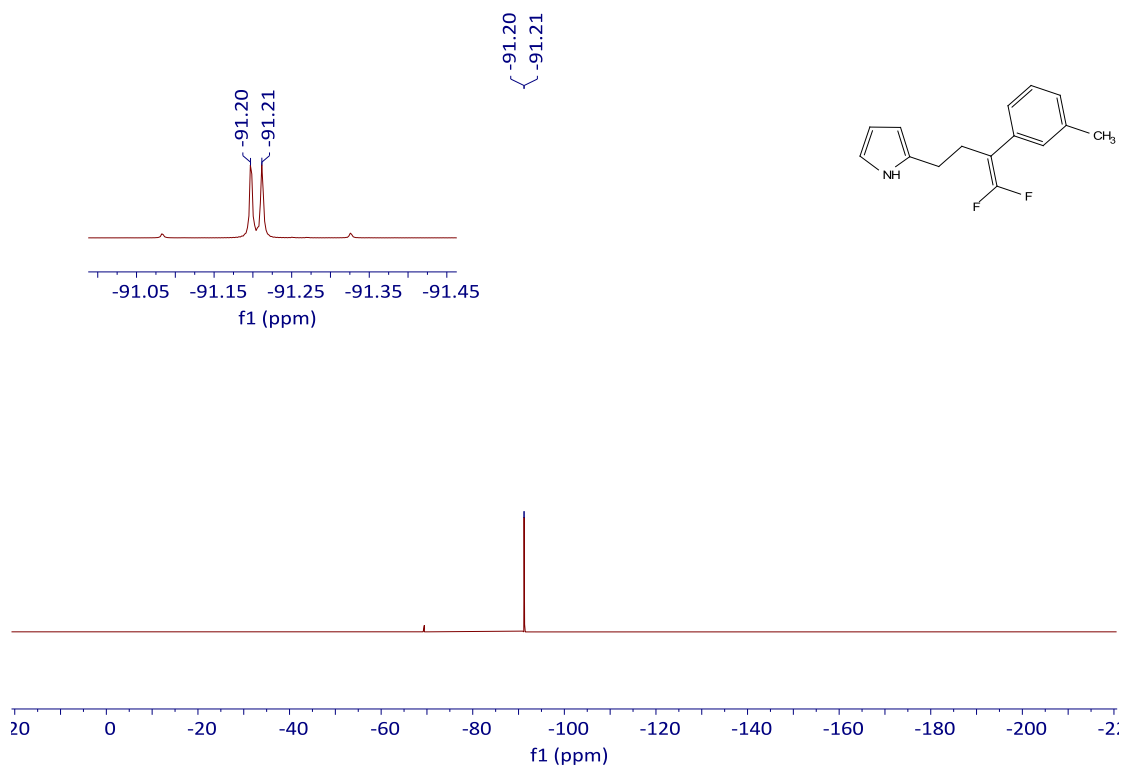
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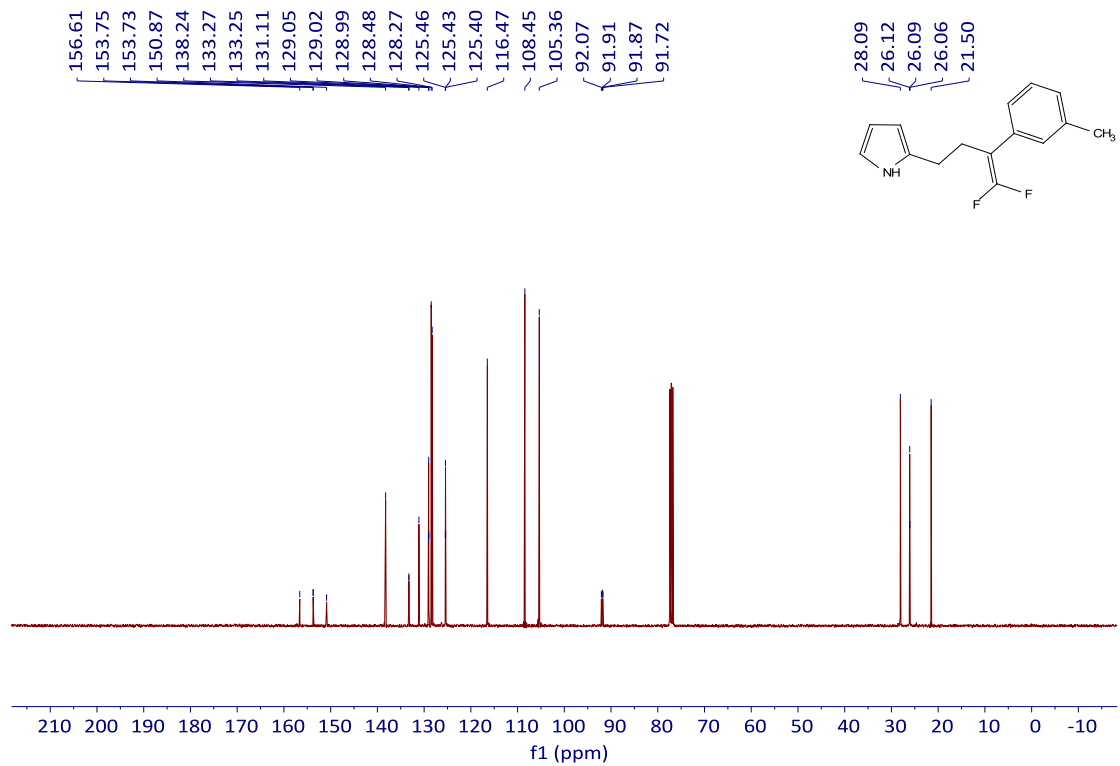
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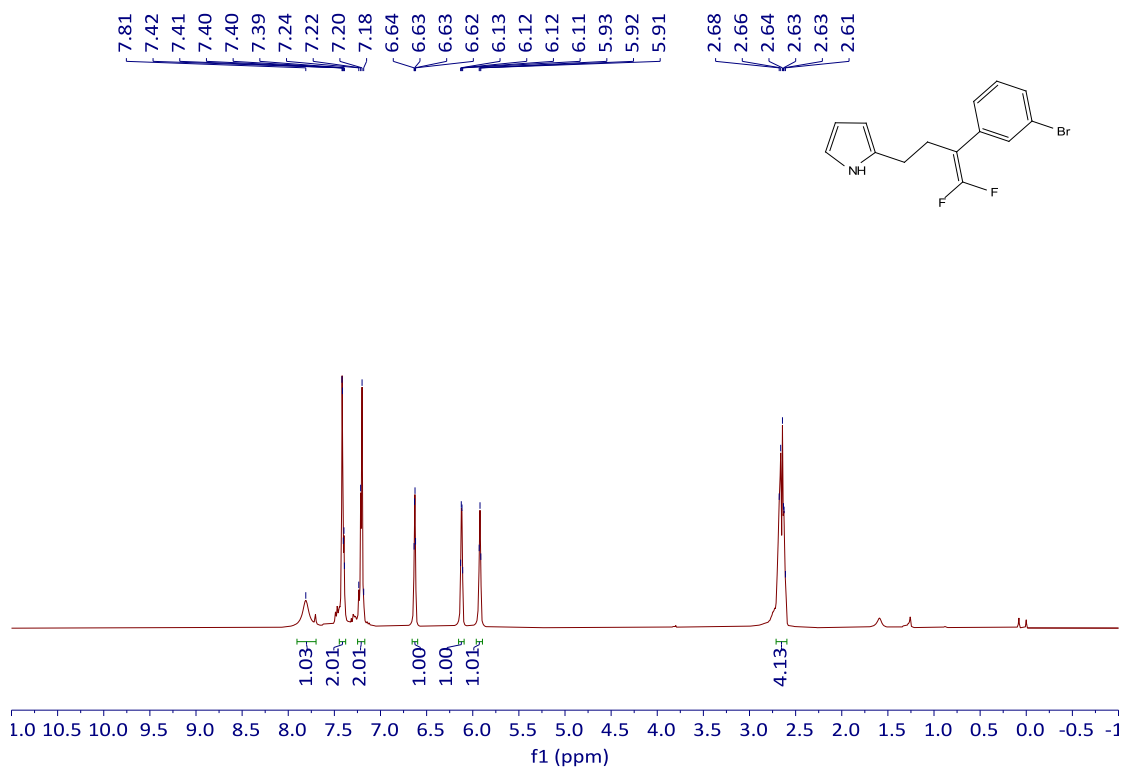
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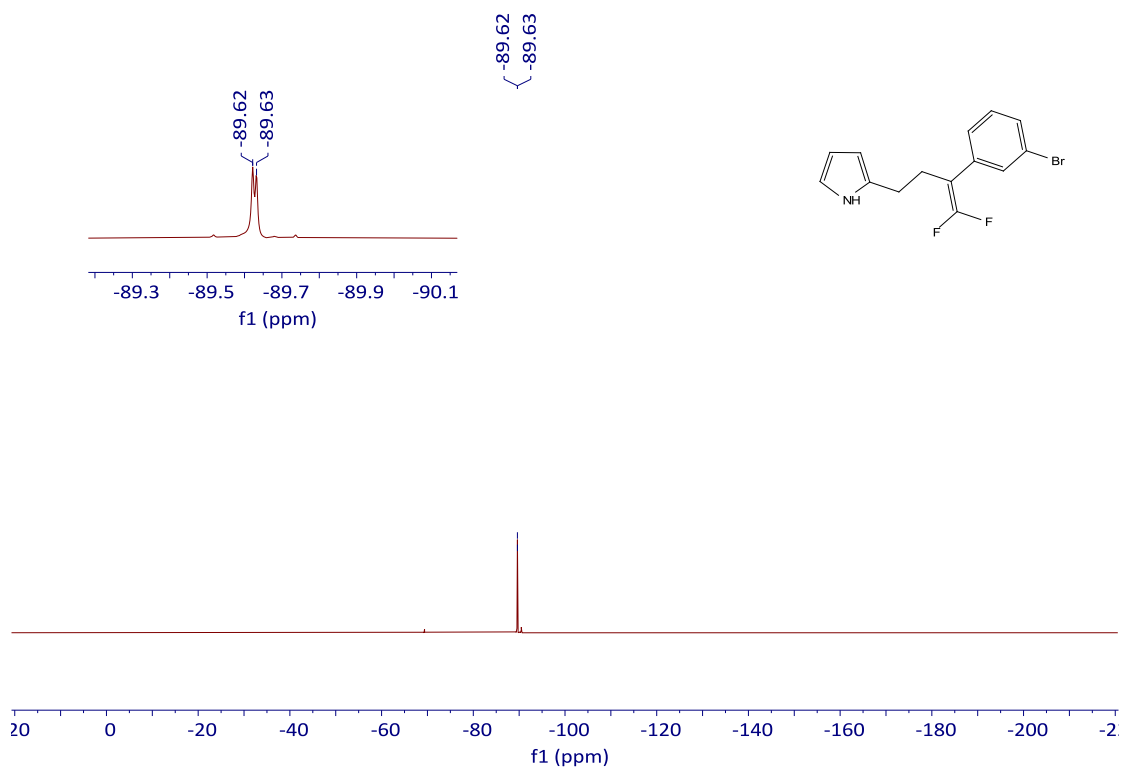
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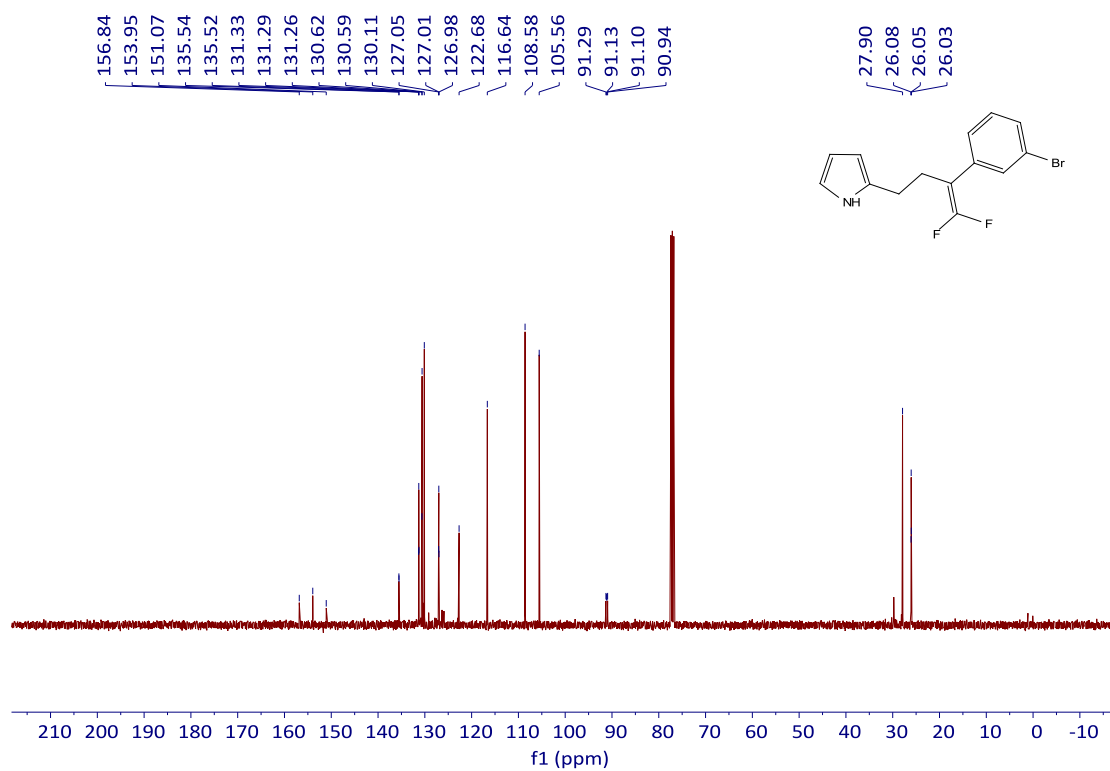
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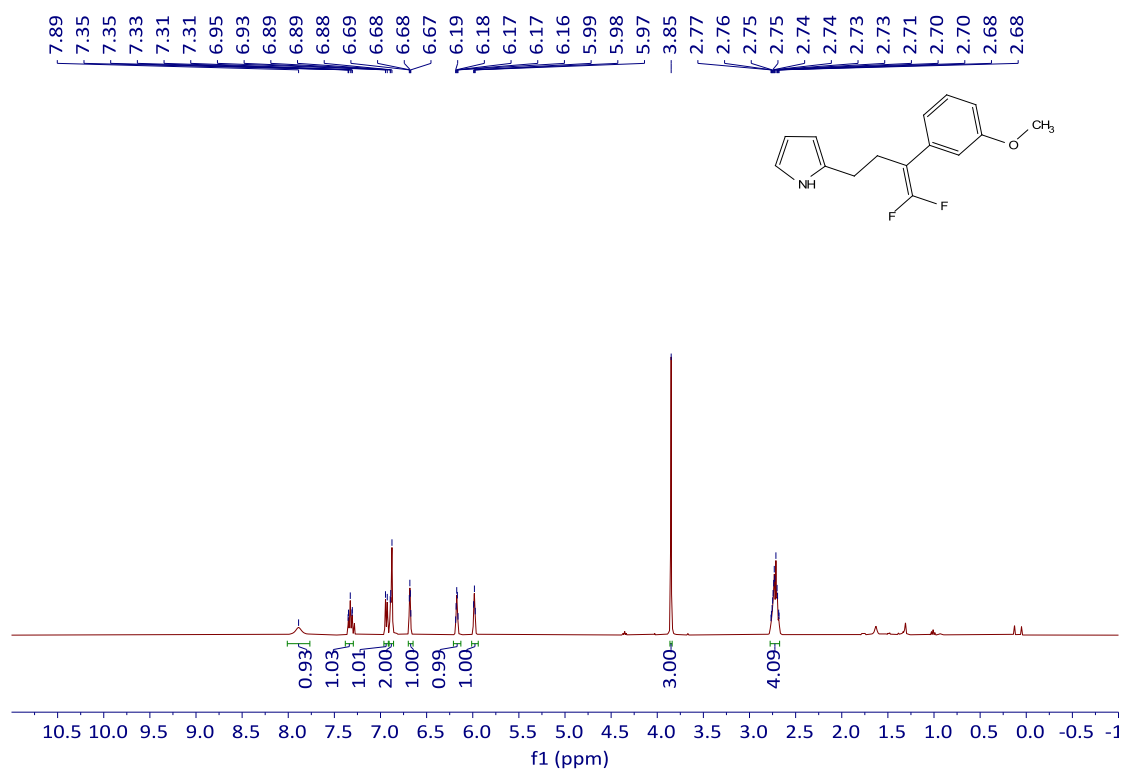
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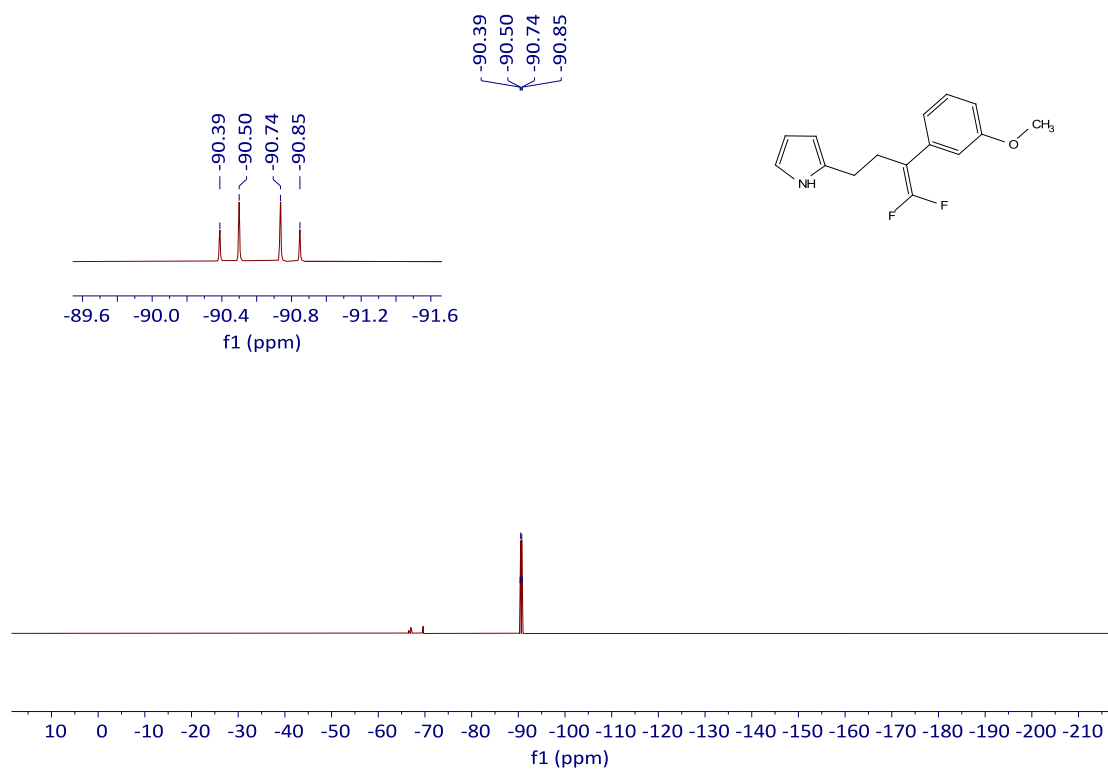
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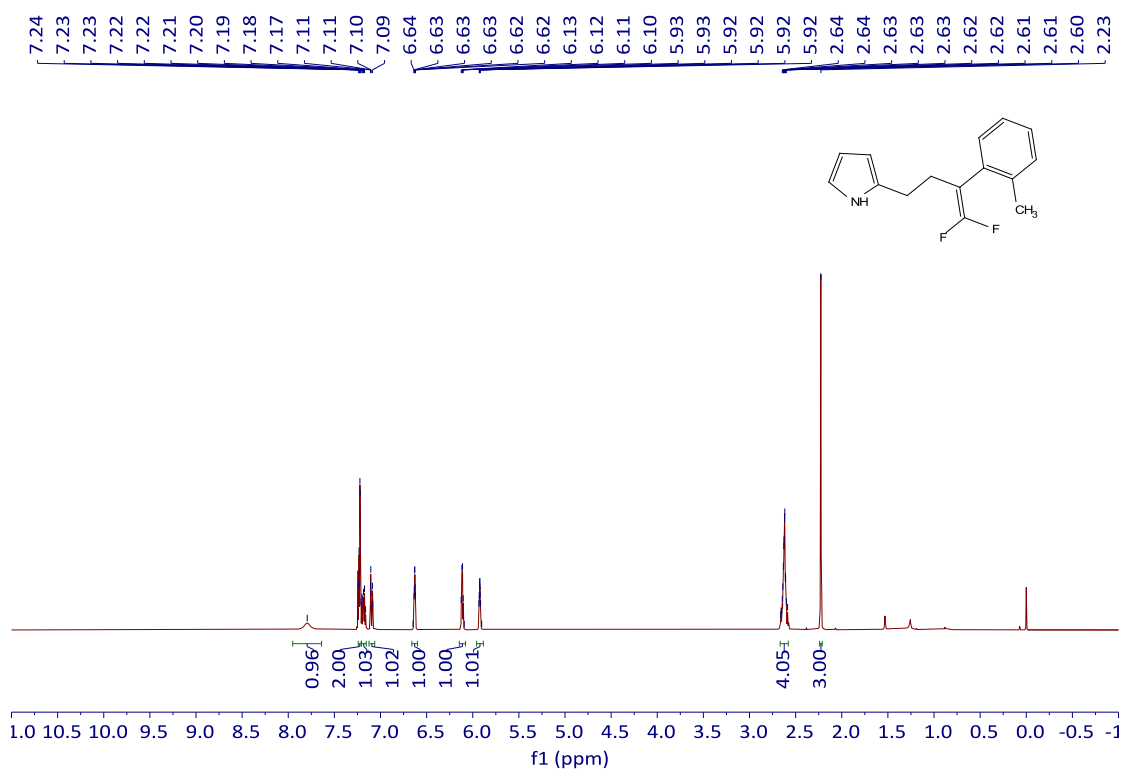
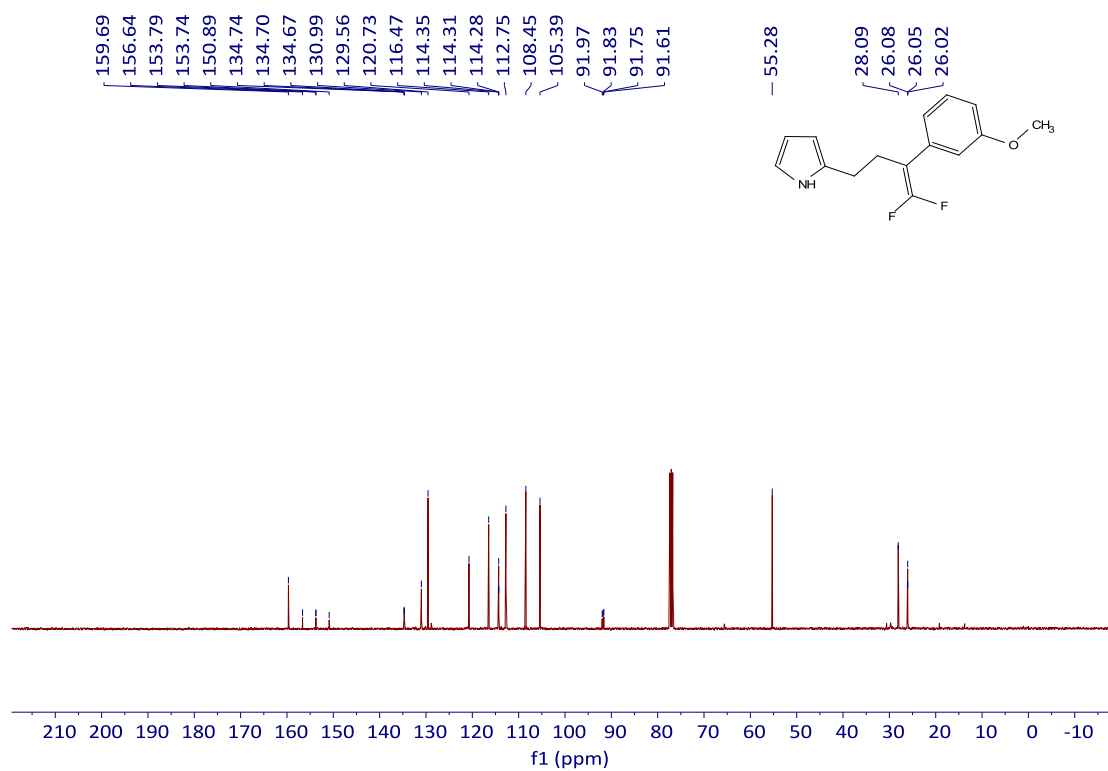
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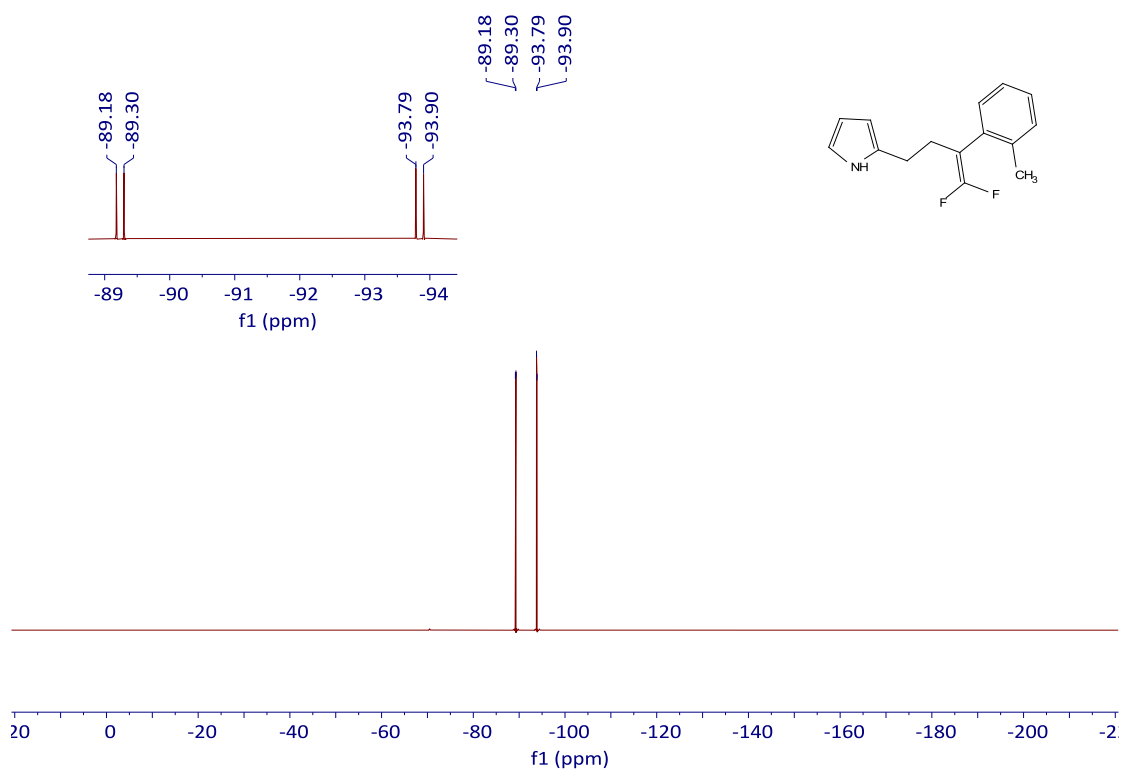
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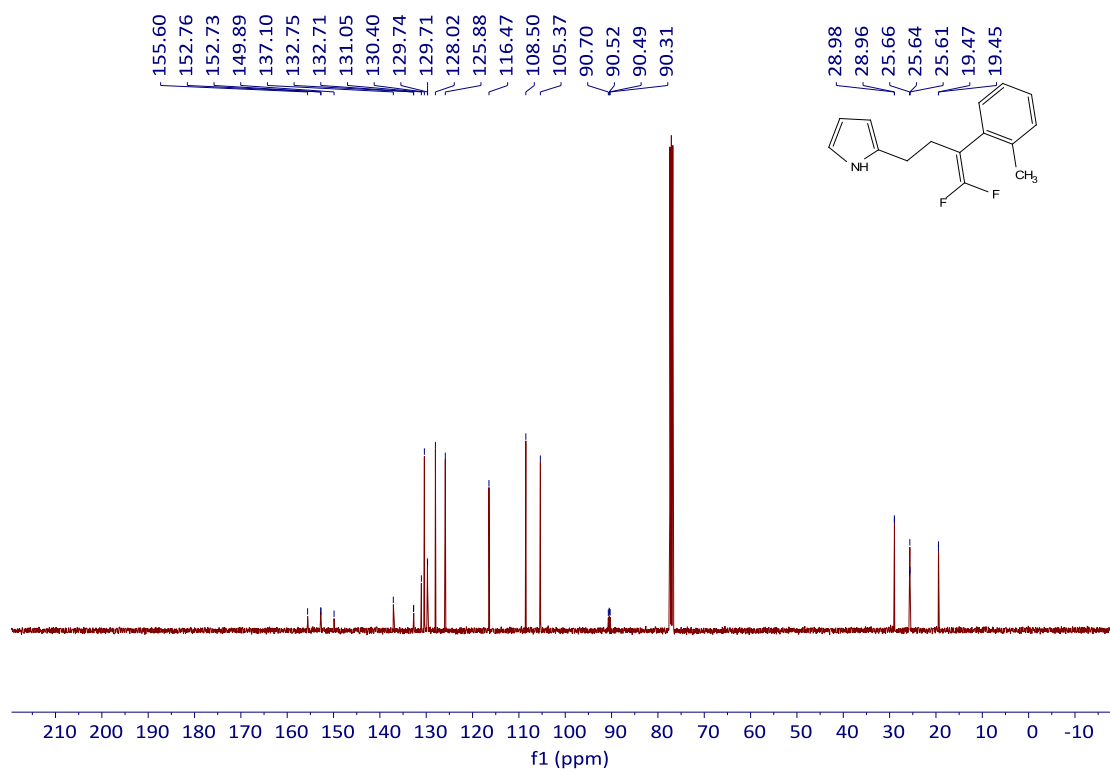
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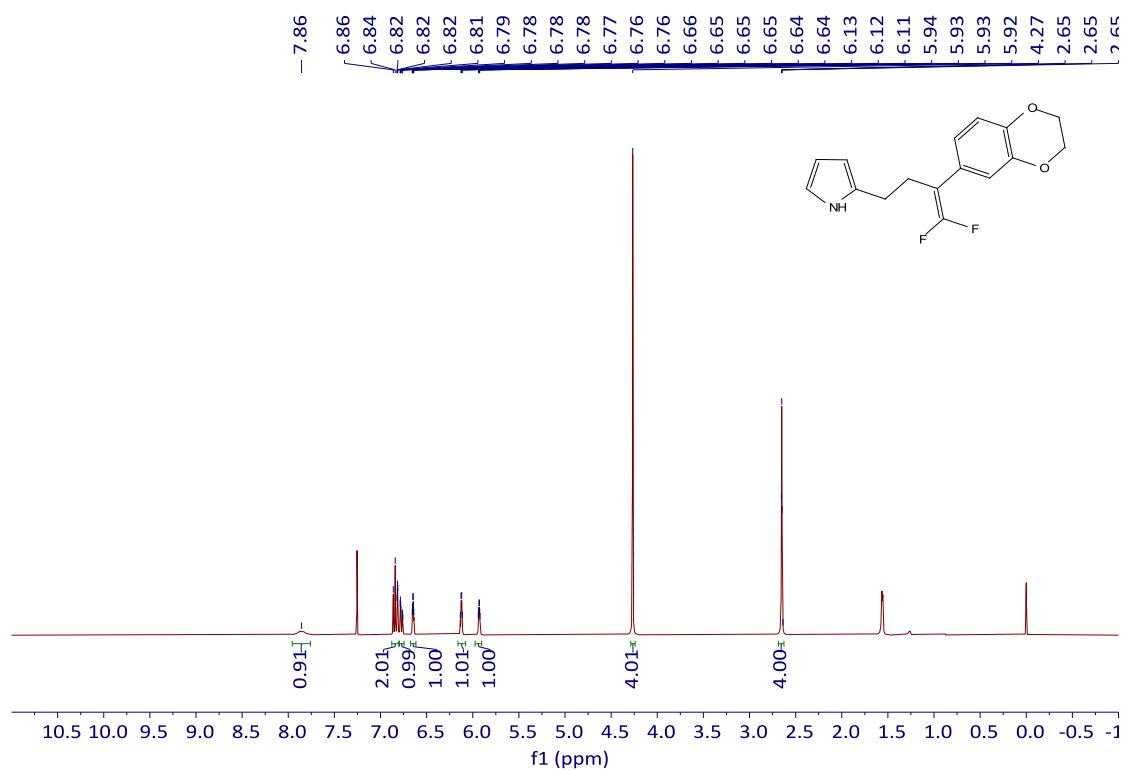
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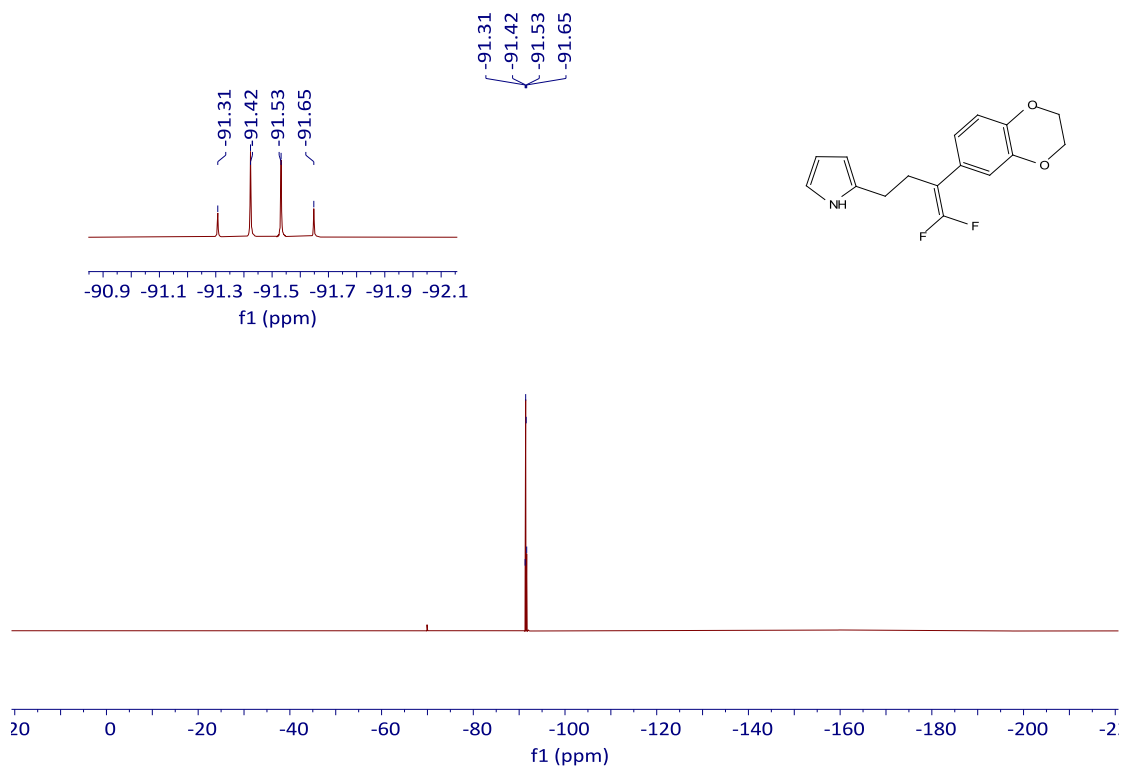
¹⁹F NMR of **3I** (376 Hz, CDCl₃)



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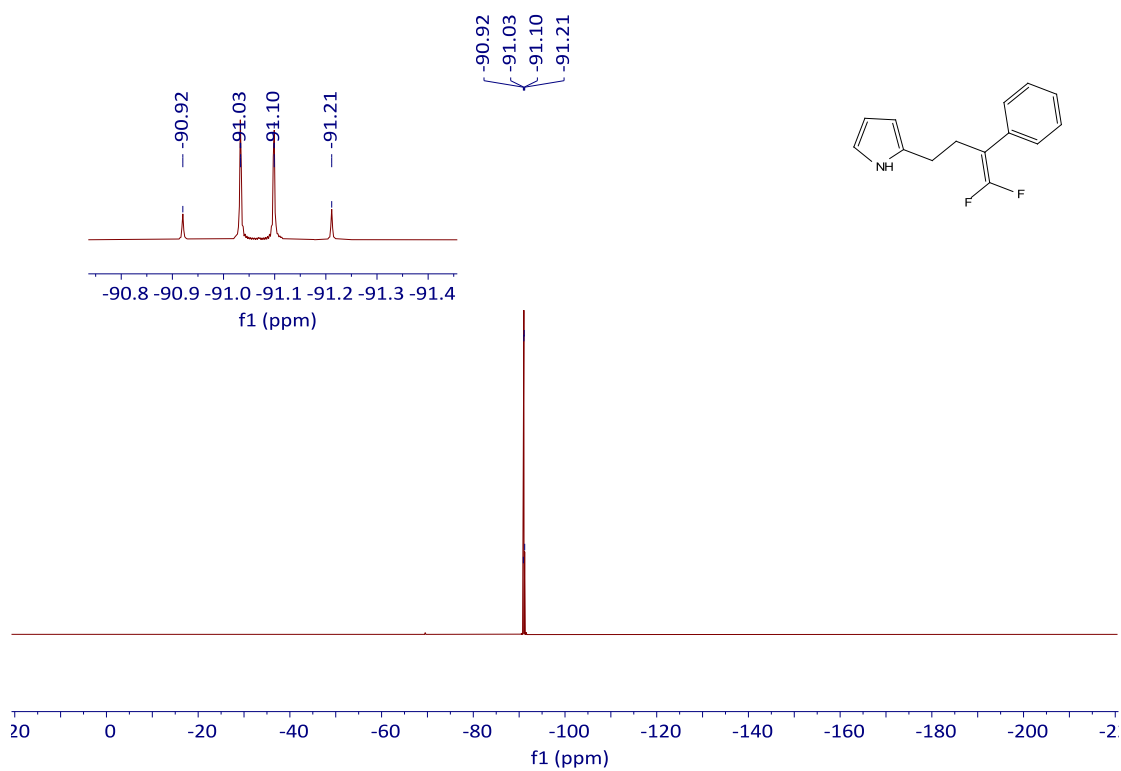


¹H NMR of **3m** (400 Hz, CDCl₃)

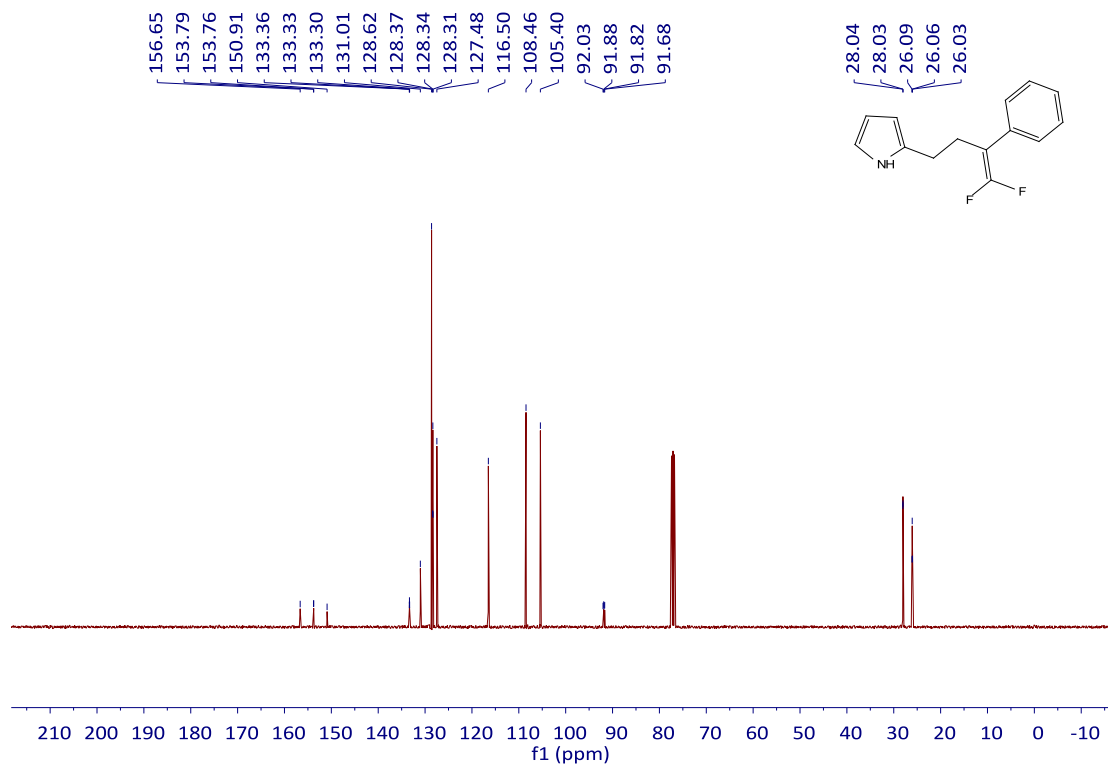


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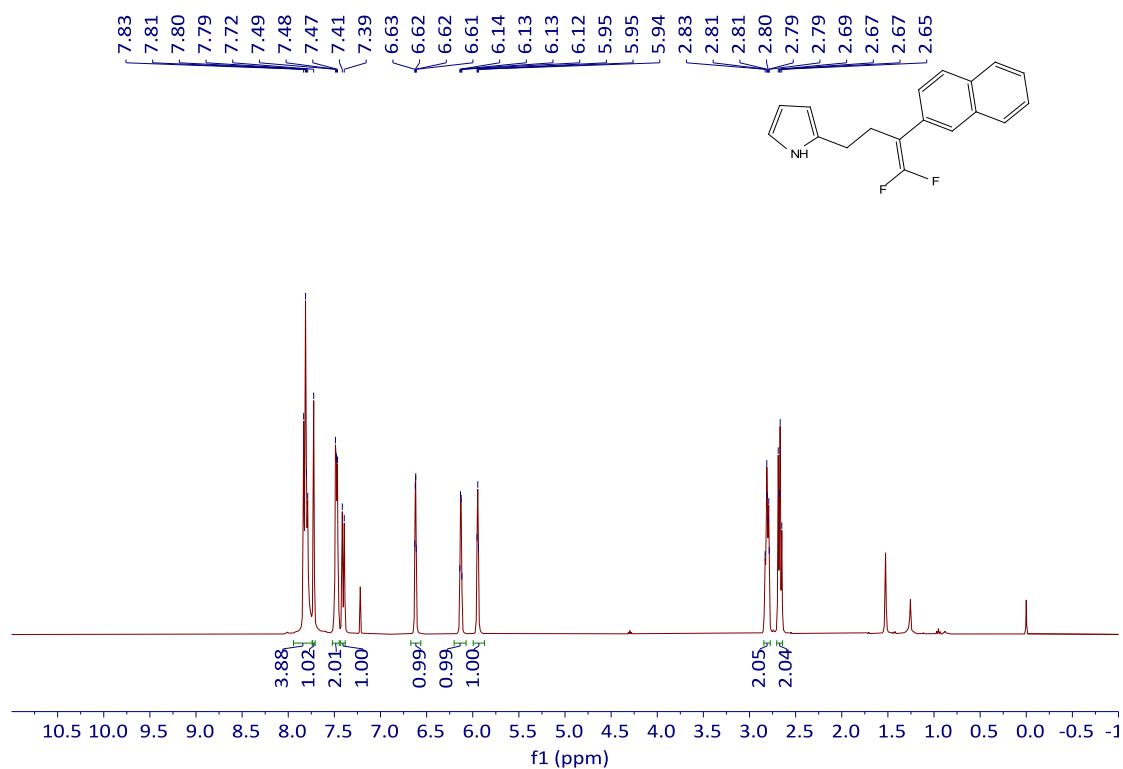
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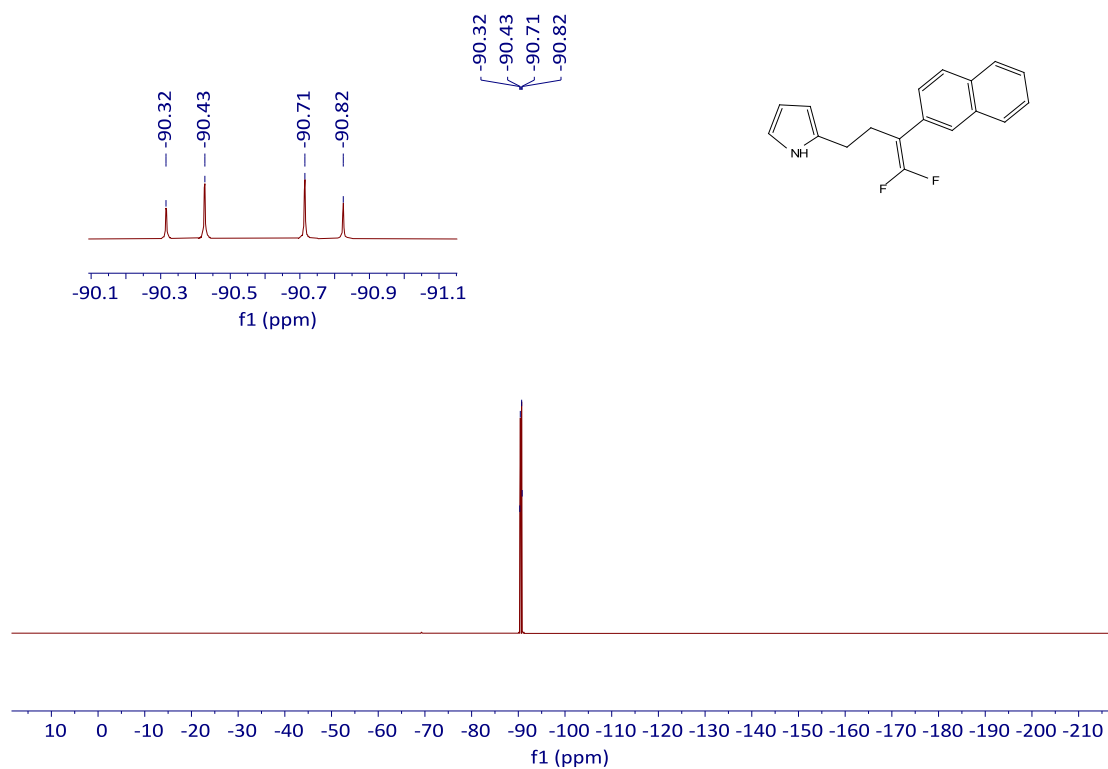
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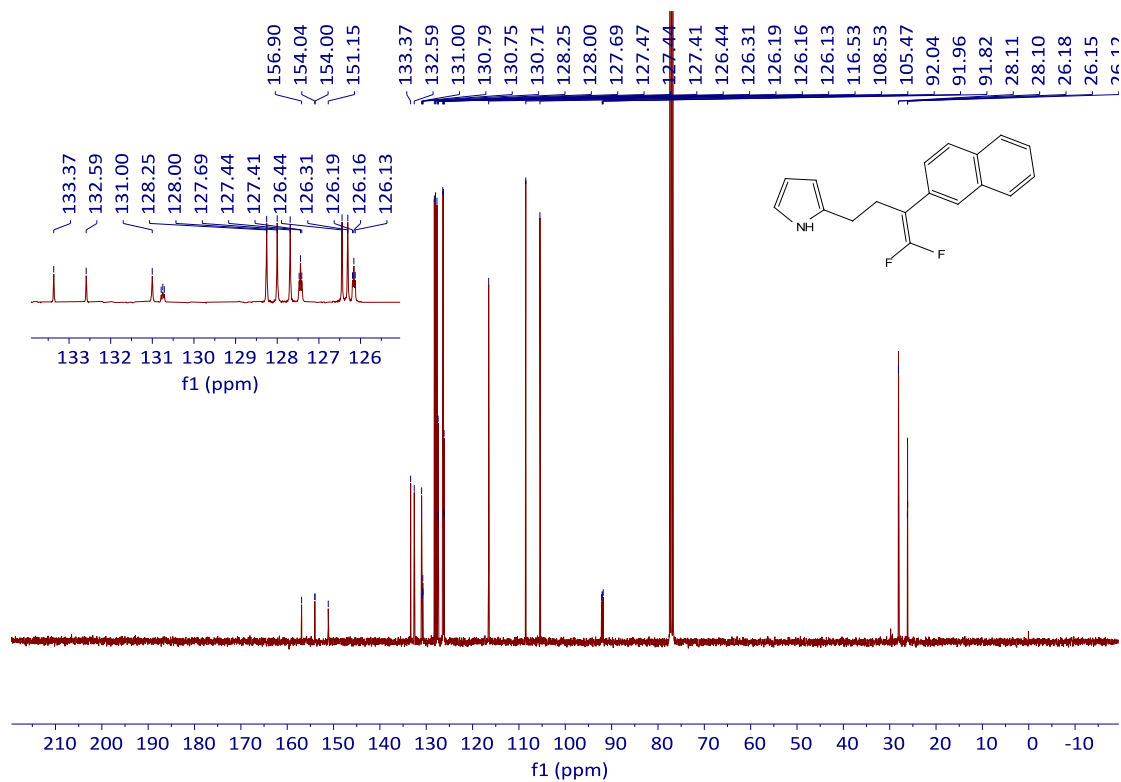
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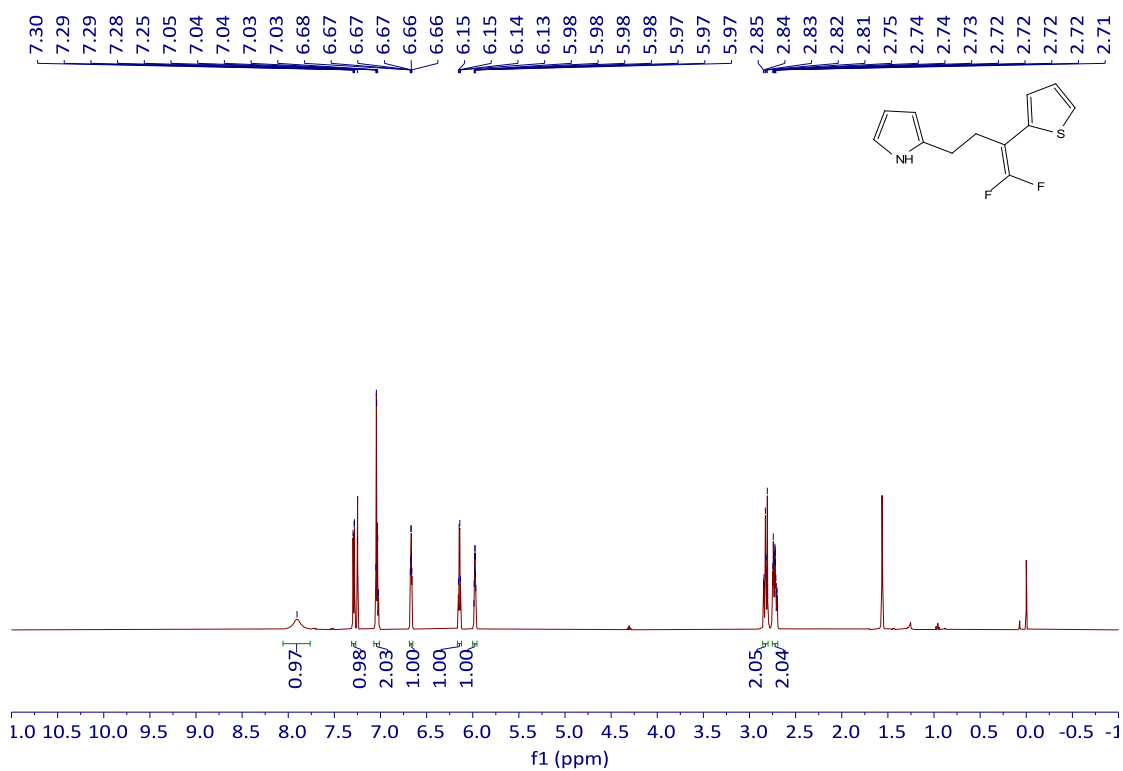
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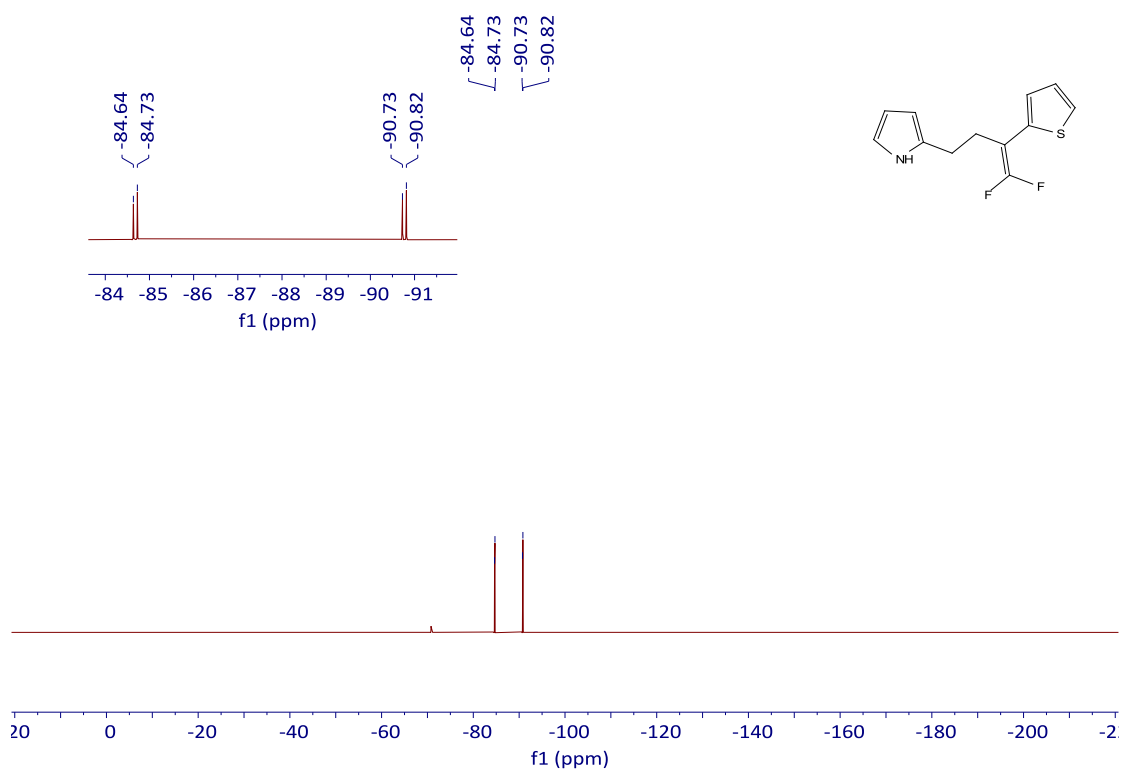
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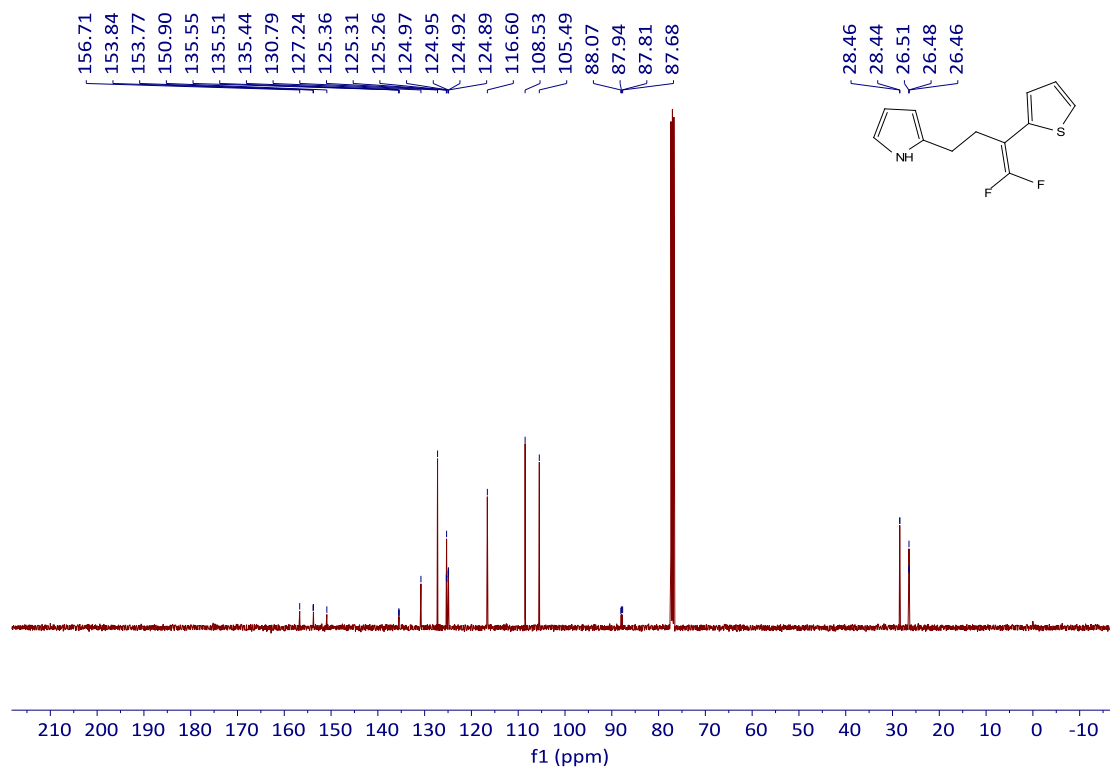
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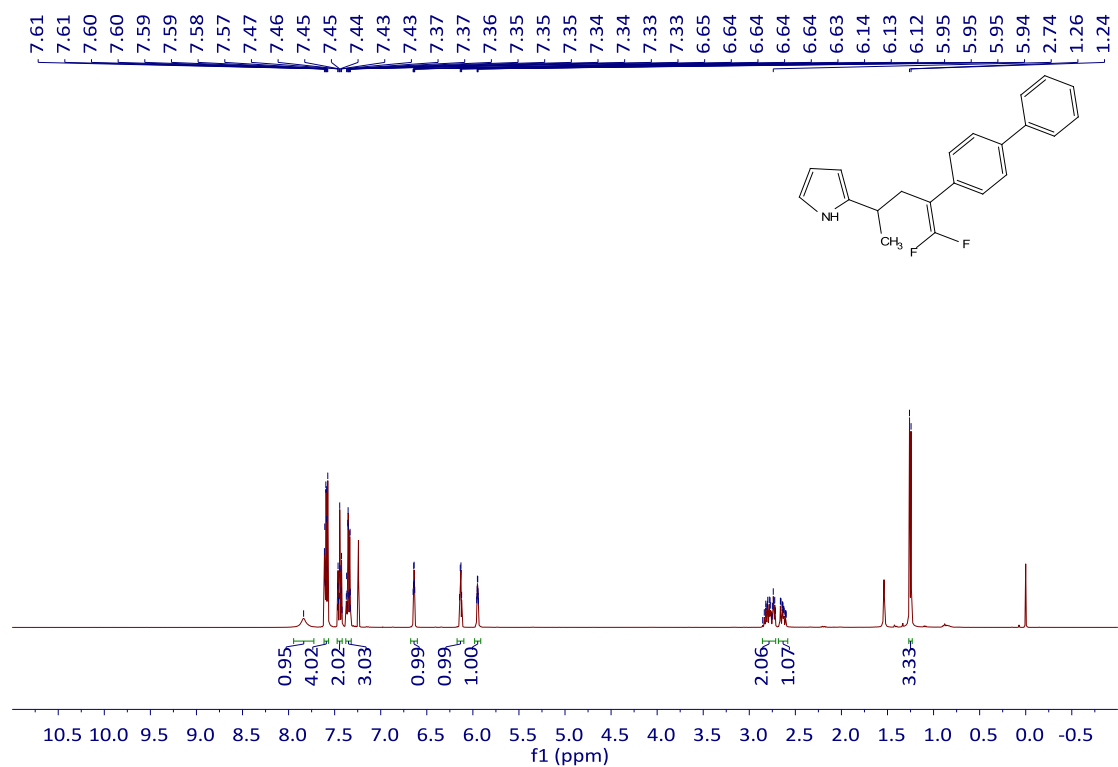
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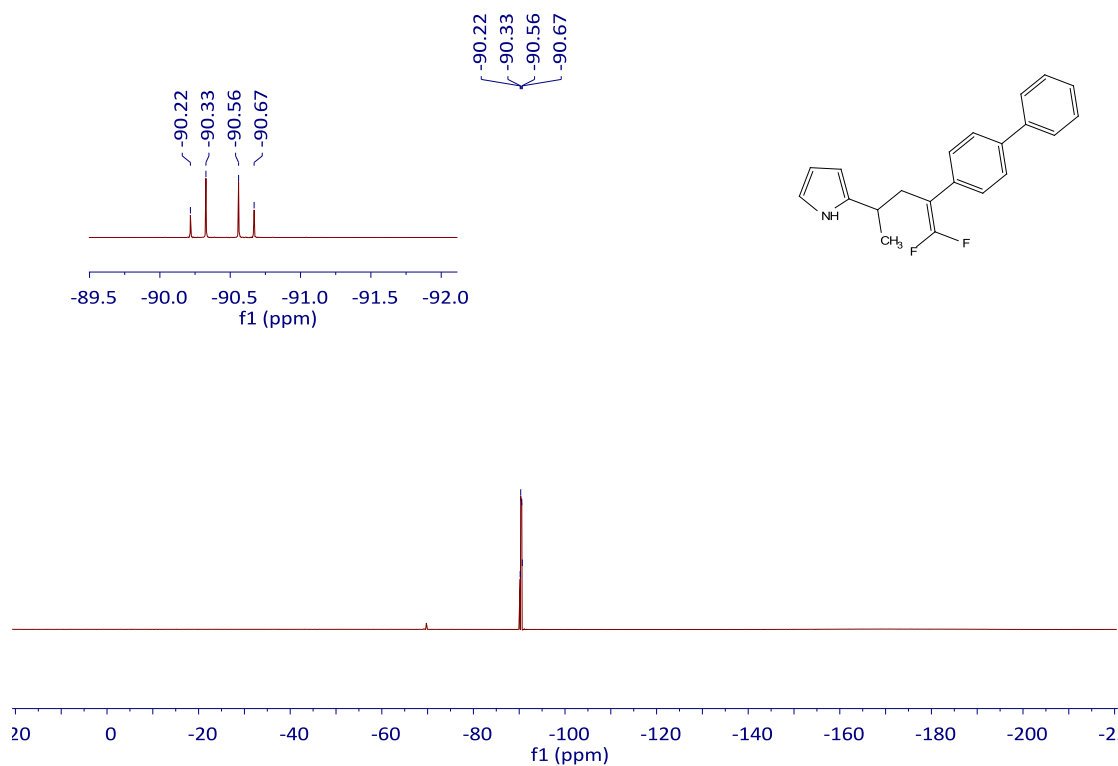
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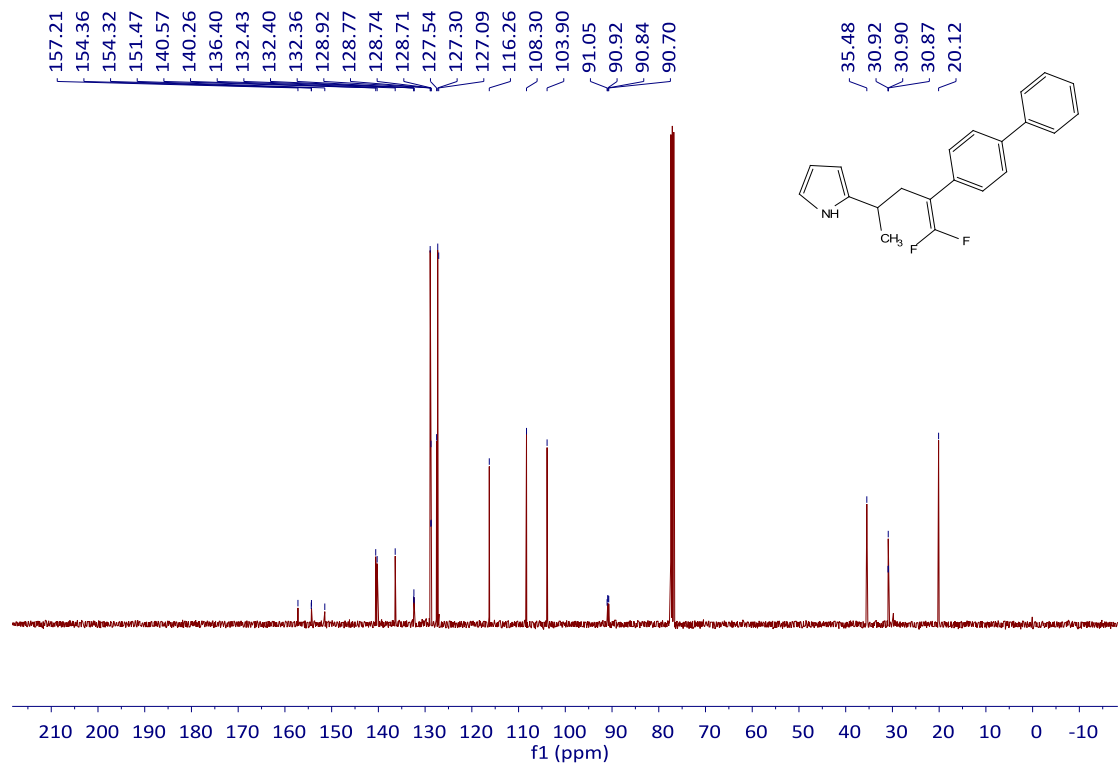
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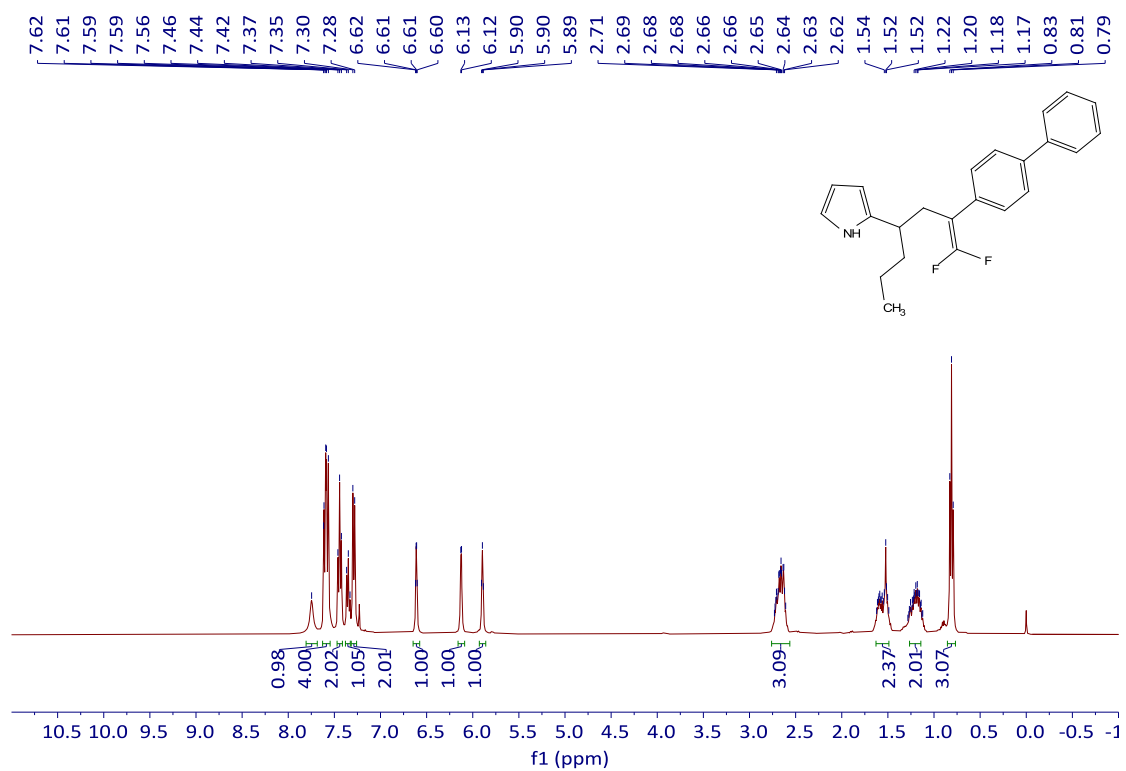
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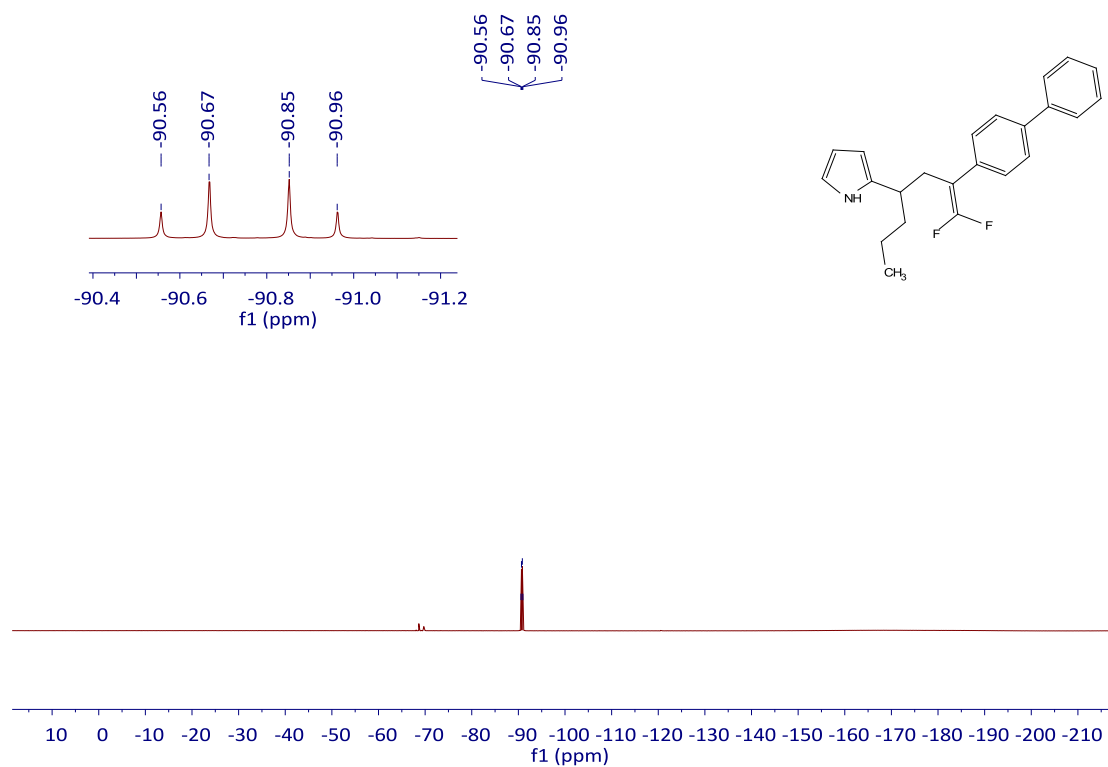
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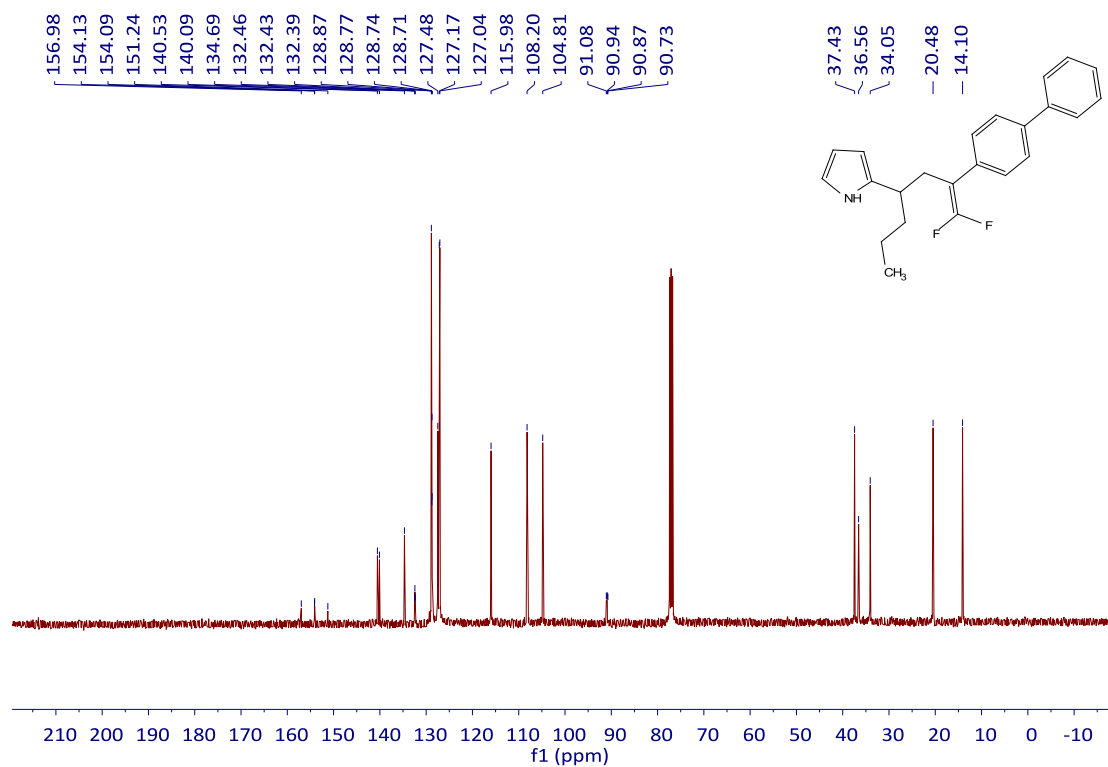
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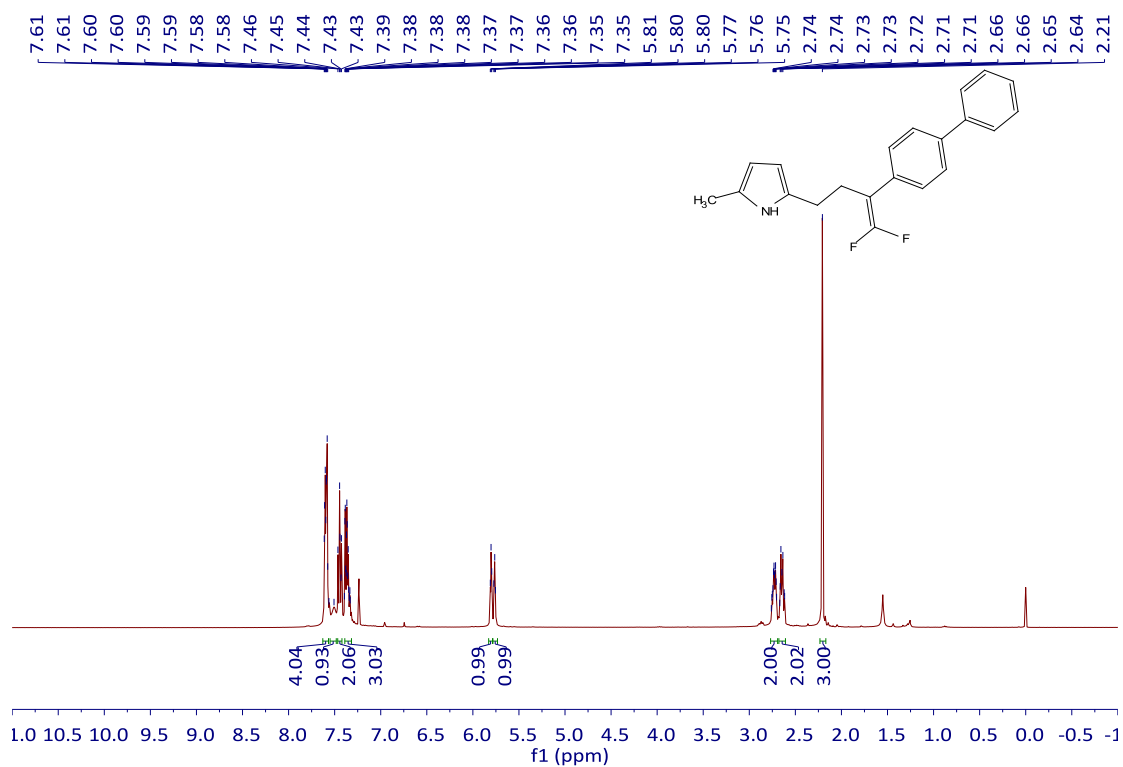
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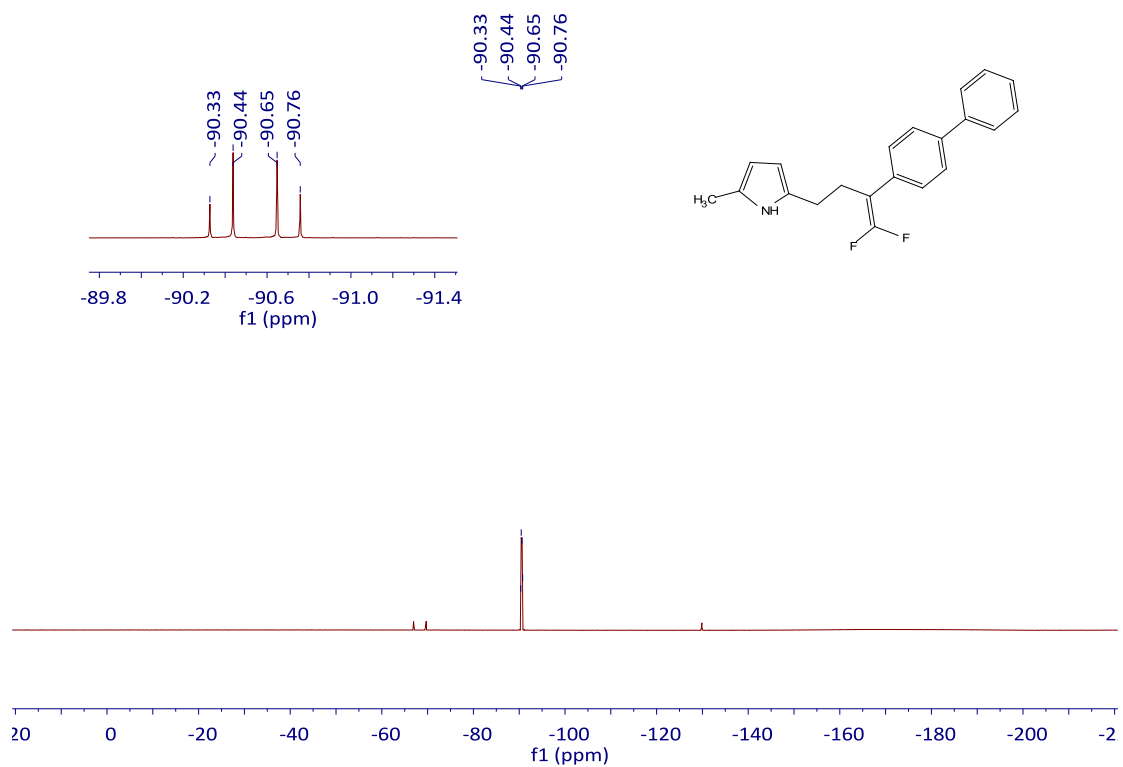
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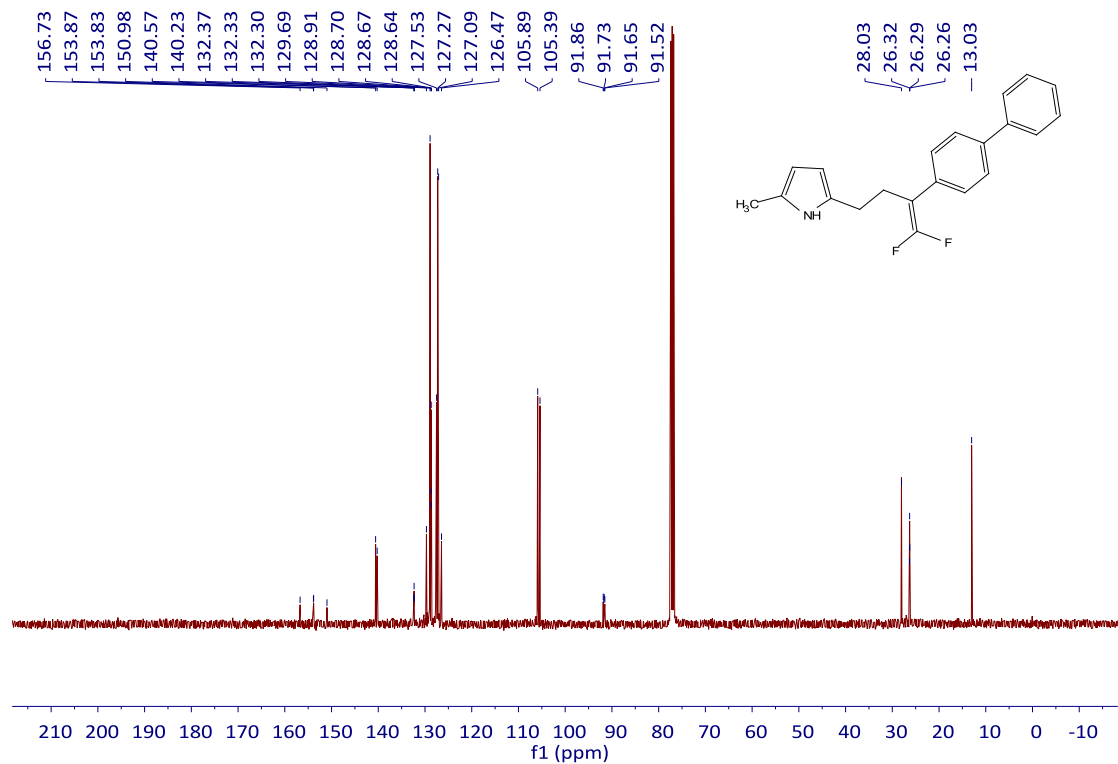
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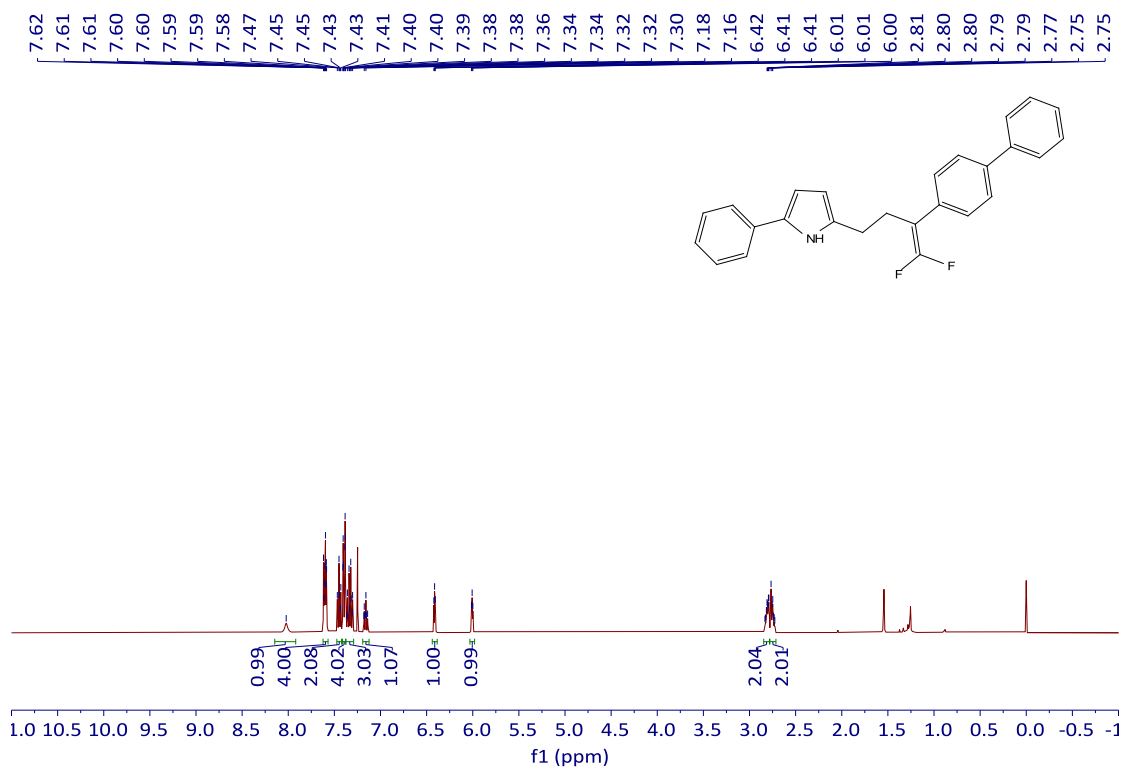
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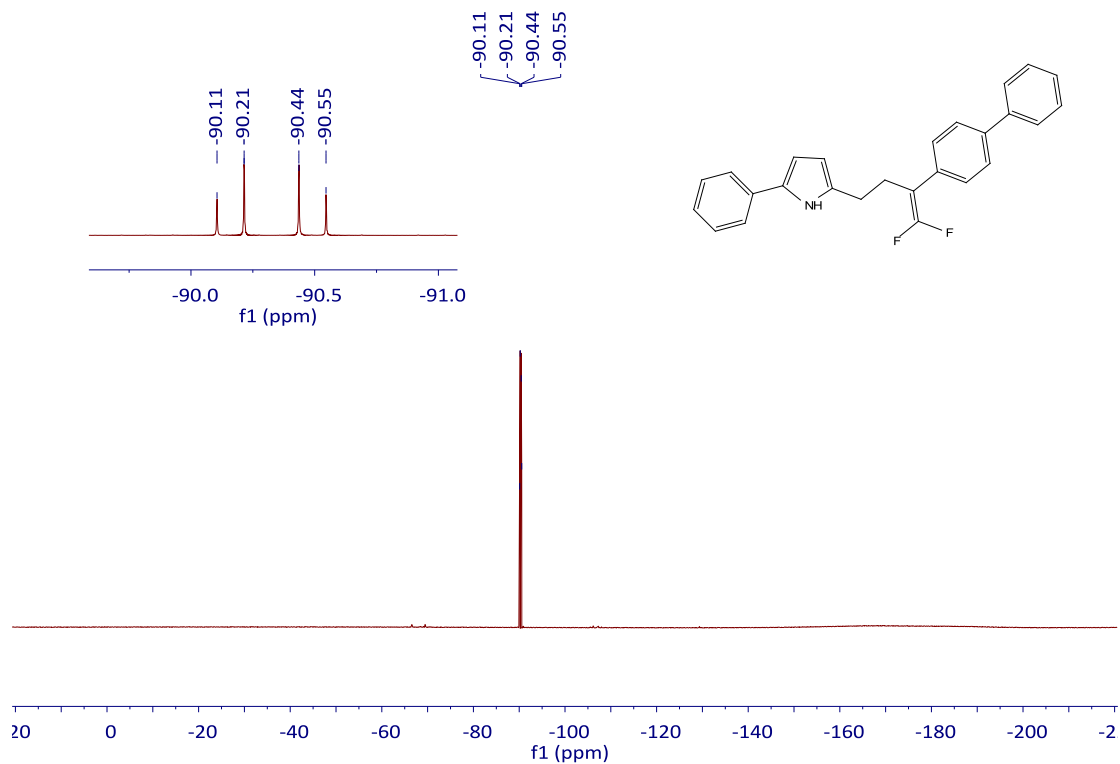
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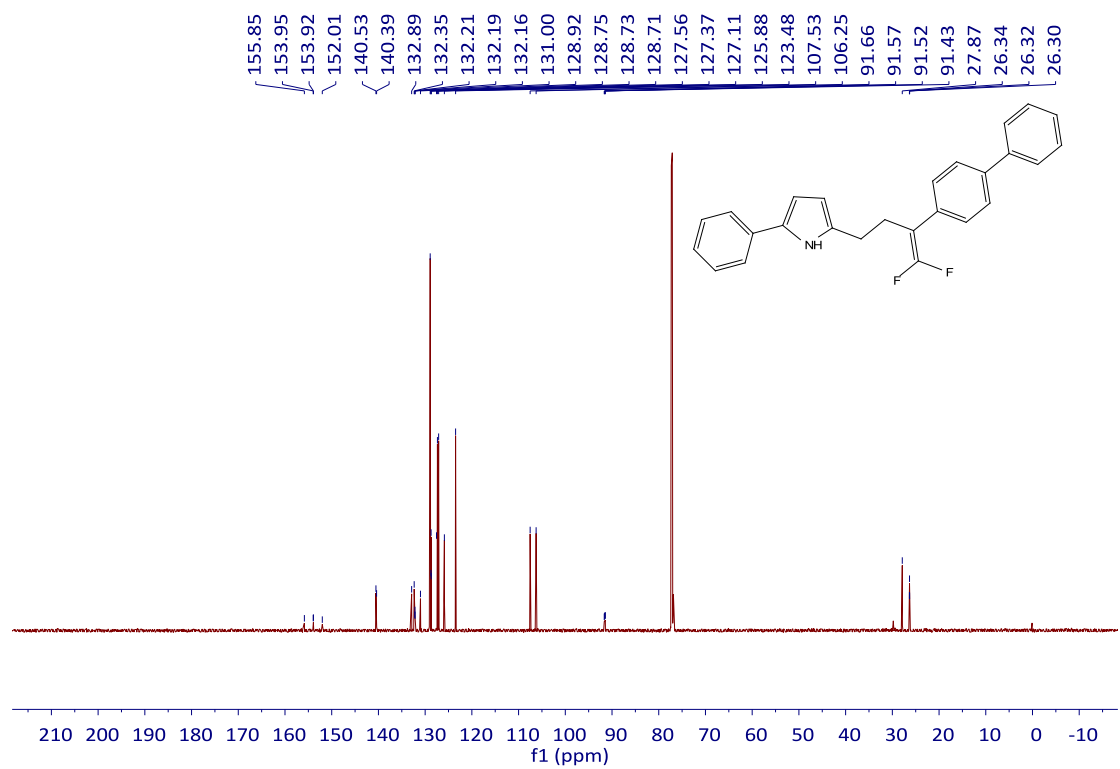
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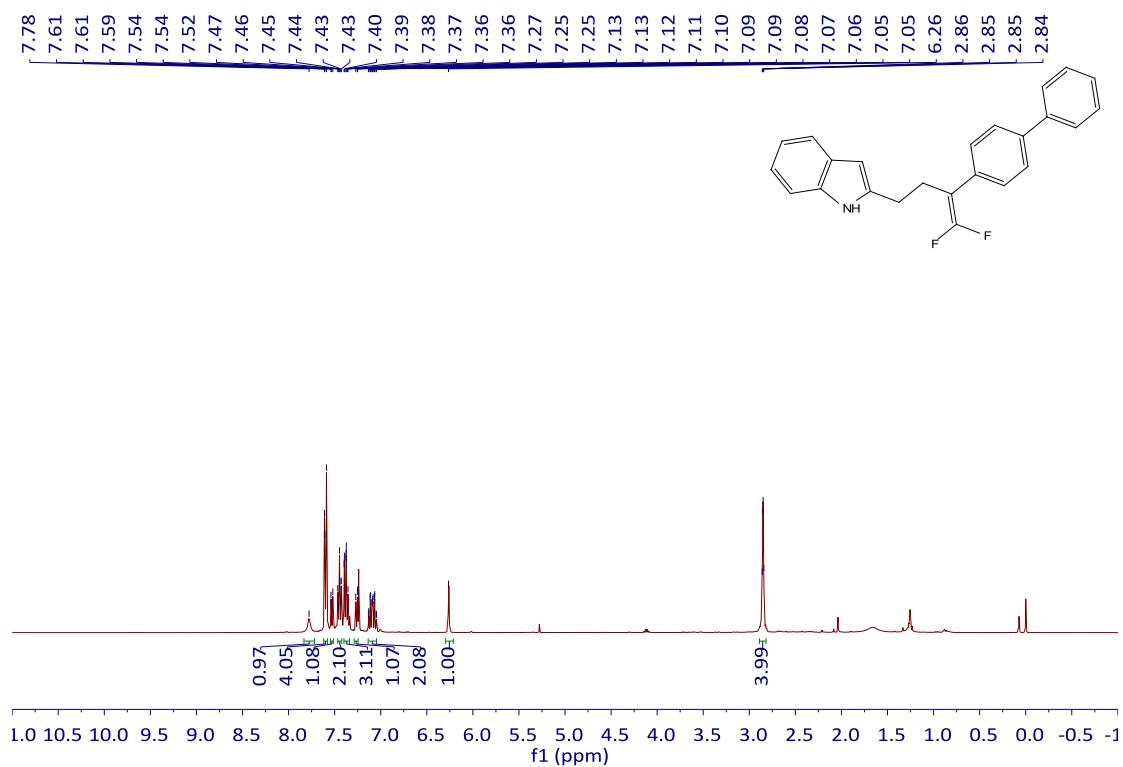
¹H NMR of **3t** (400 Hz, CDCl₃)



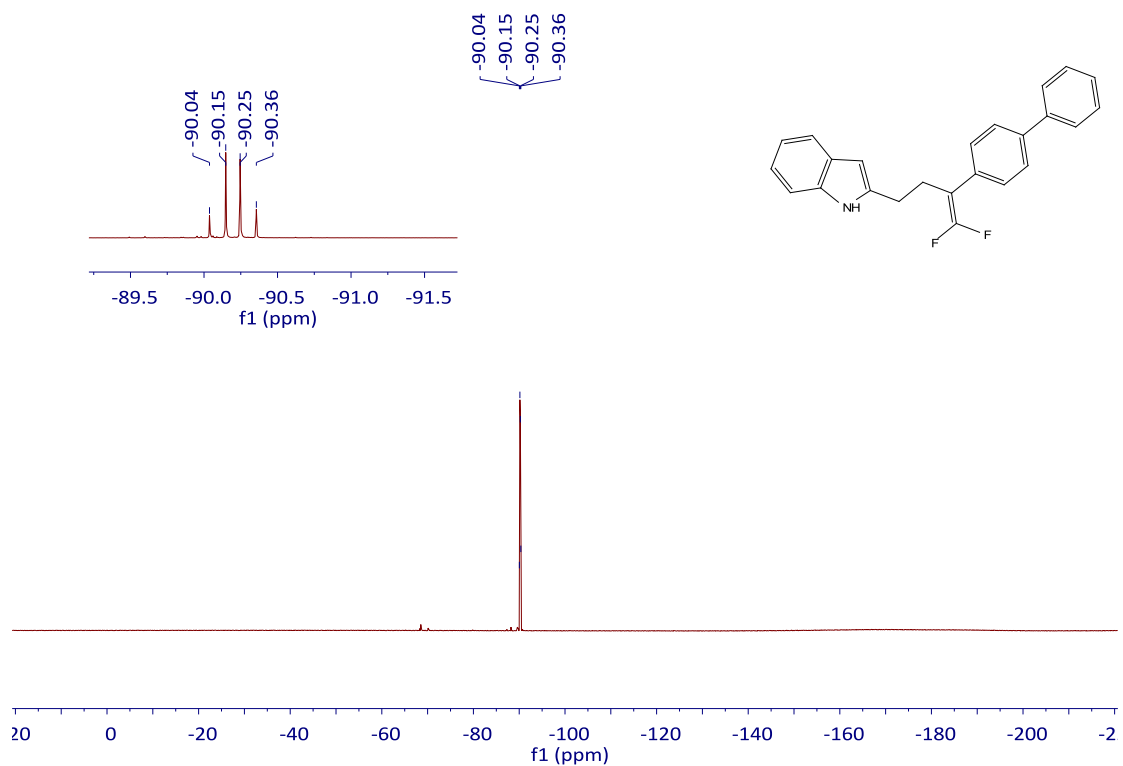
¹⁹F NMR of **3t** (376 Hz, CDCl₃)



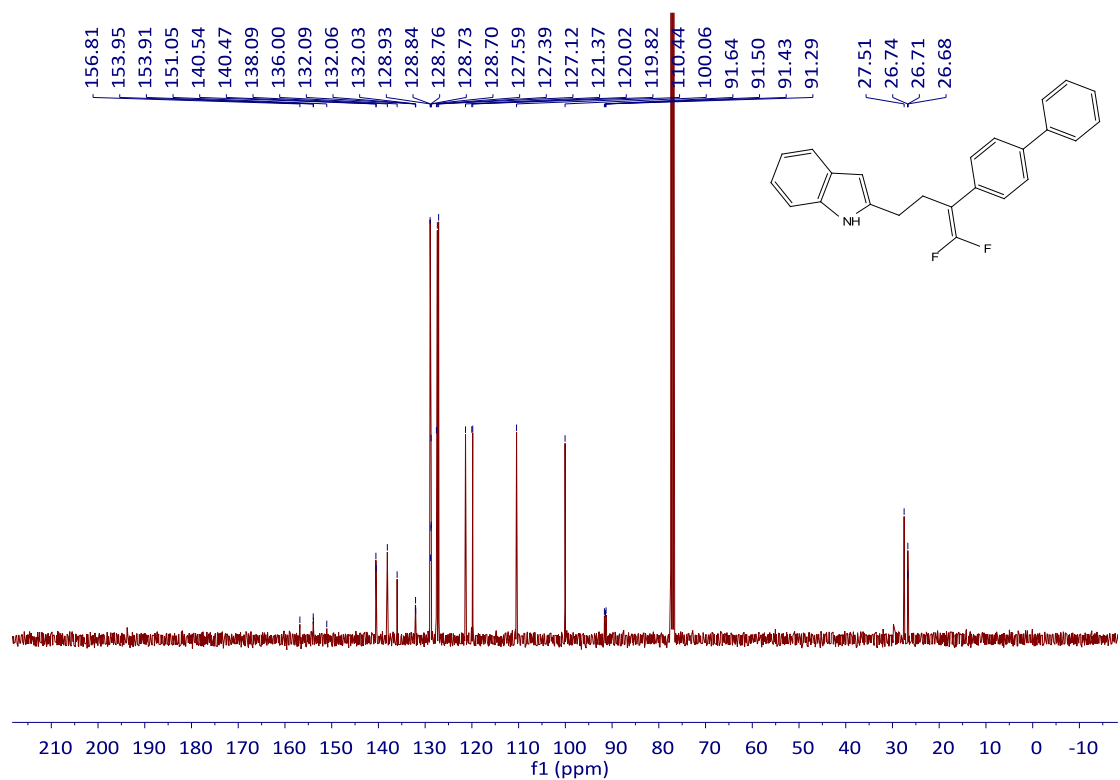
¹³C{¹H} NMR of **3t** (150 Hz, CDCl₃)



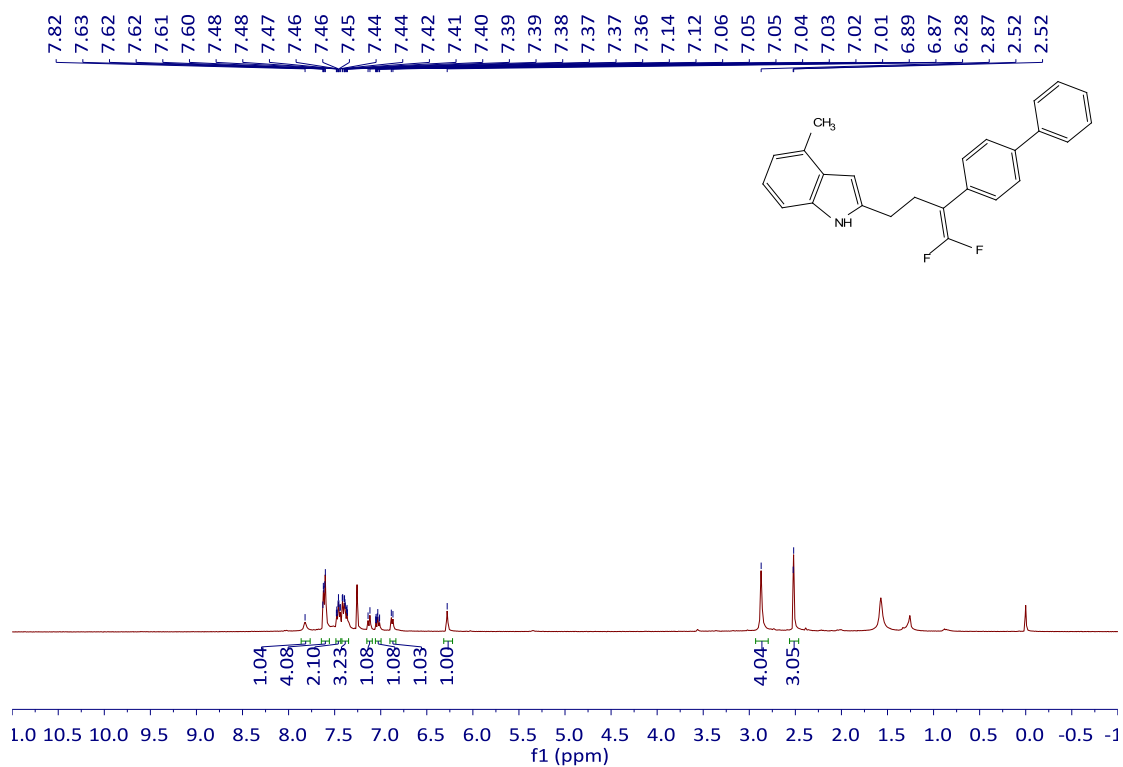
¹H NMR of **3u** (400 Hz, CDCl₃)



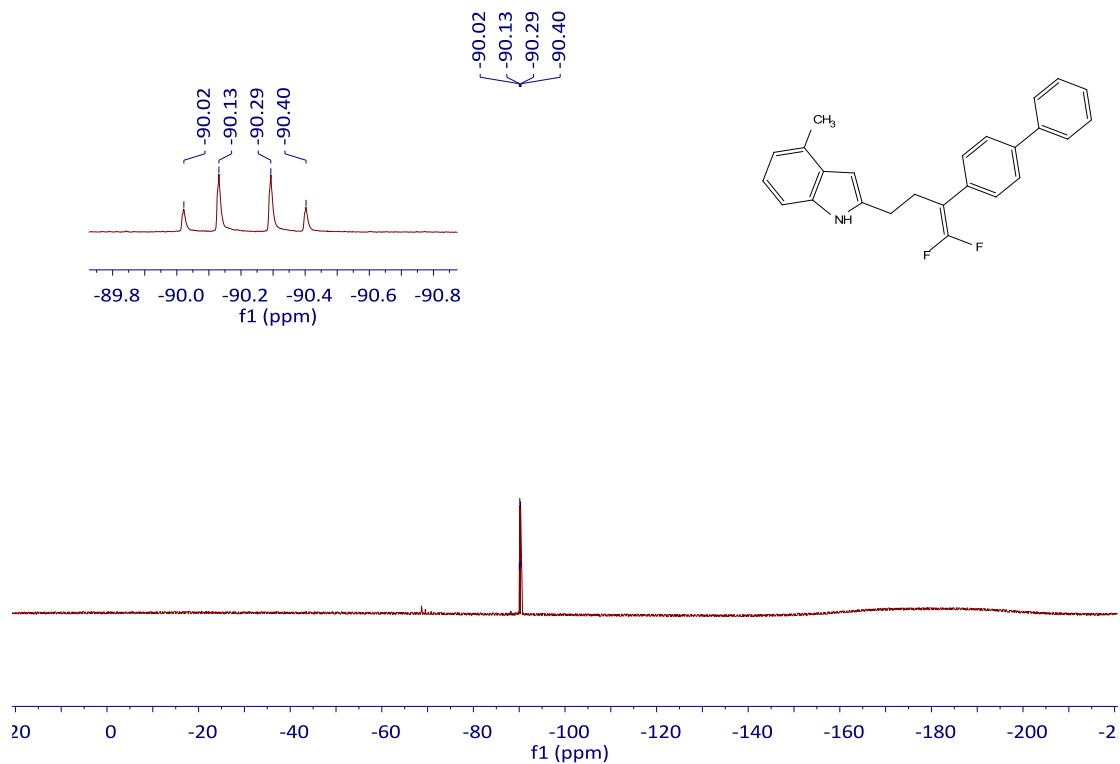
¹⁹F NMR of **3u** (376 Hz, CDCl₃)



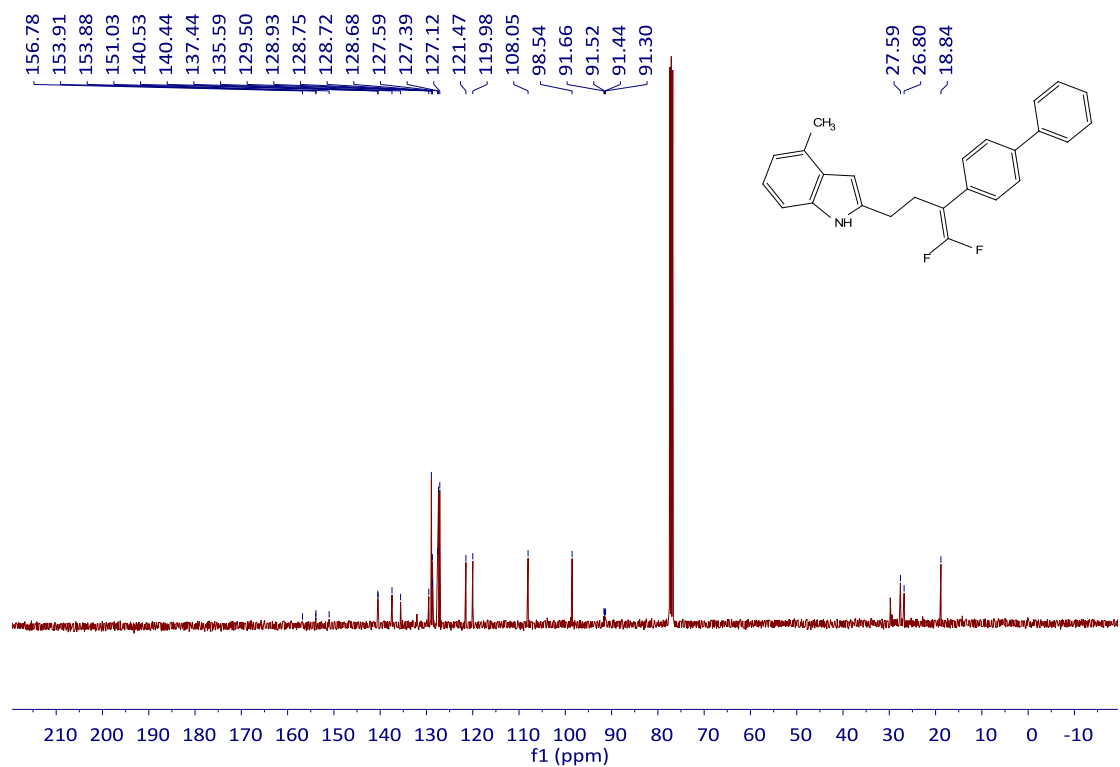
$^{13}\text{C}\{^1\text{H}\}$ NMR of **3u** (100 Hz, CDCl_3)



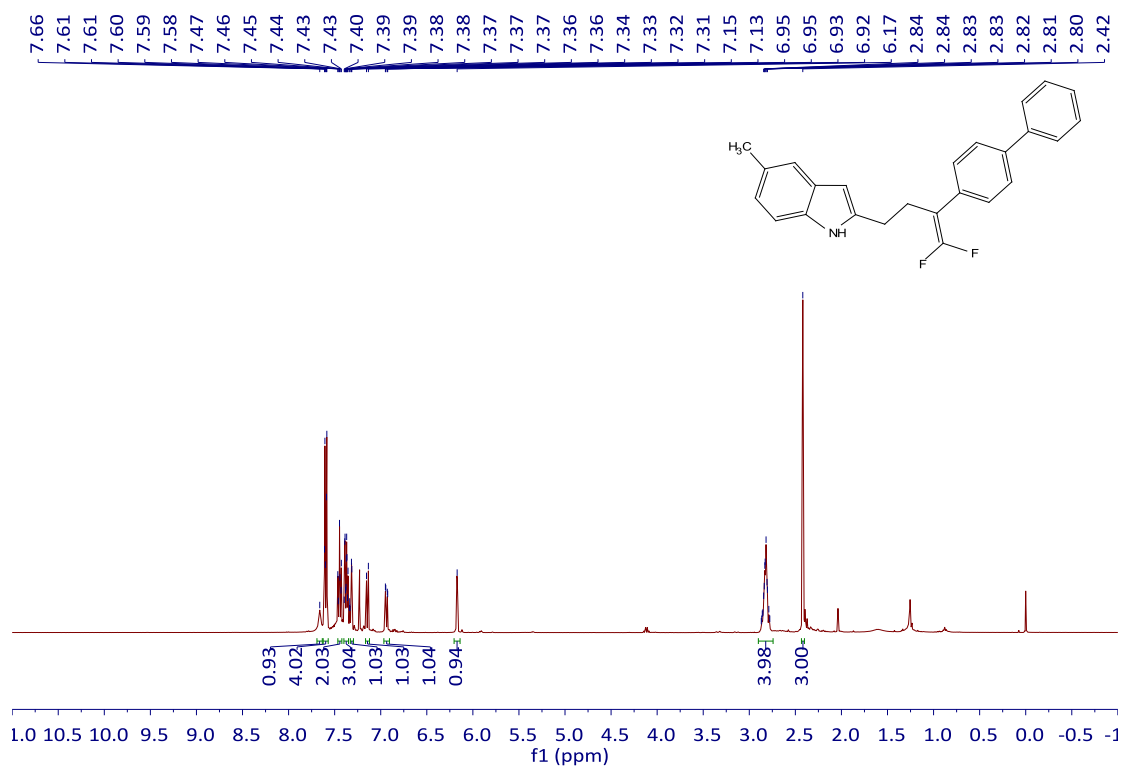
^1H NMR of **3v** (400 Hz, CDCl_3)



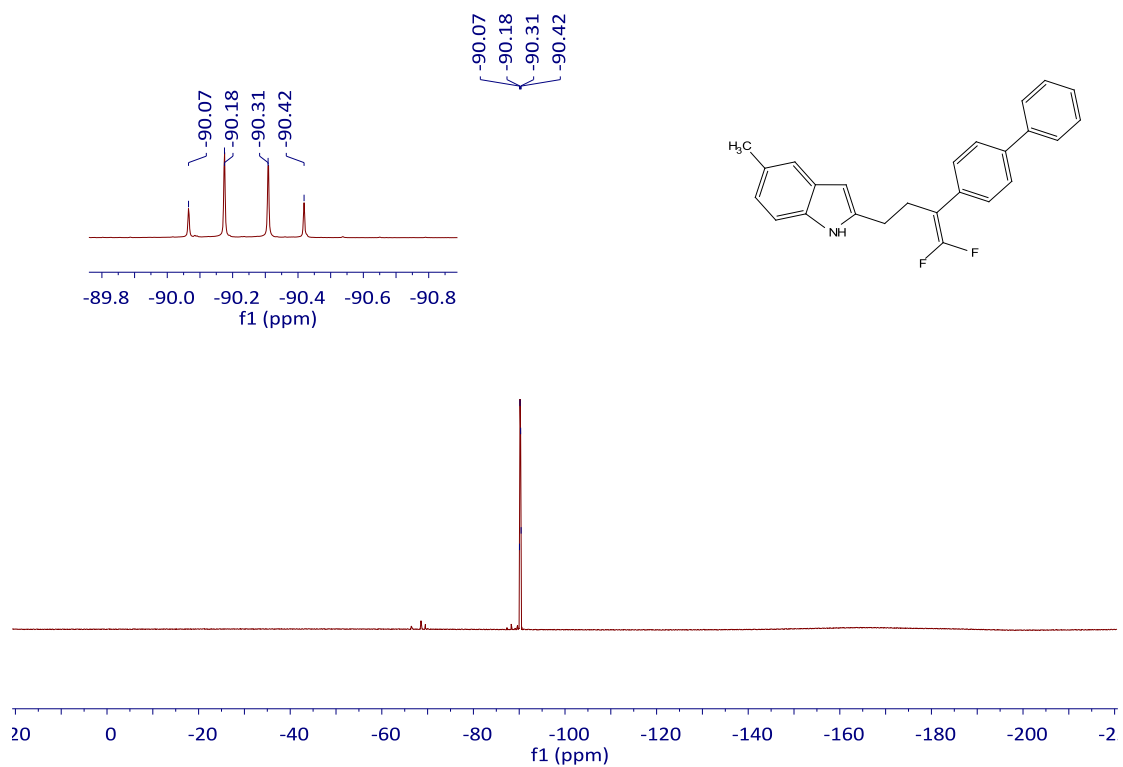
¹⁹F NMR of **3v** (376 Hz, CDCl₃)



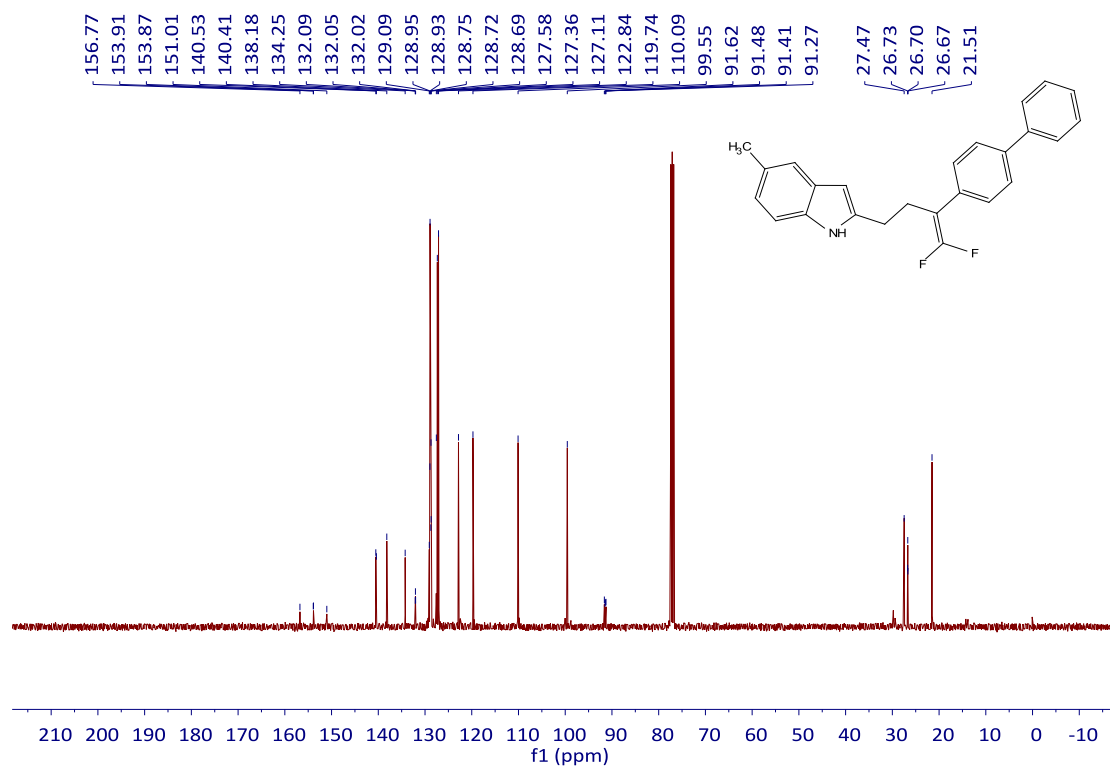
¹³C{¹H} NMR of **3v** (100 Hz, CDCl₃)



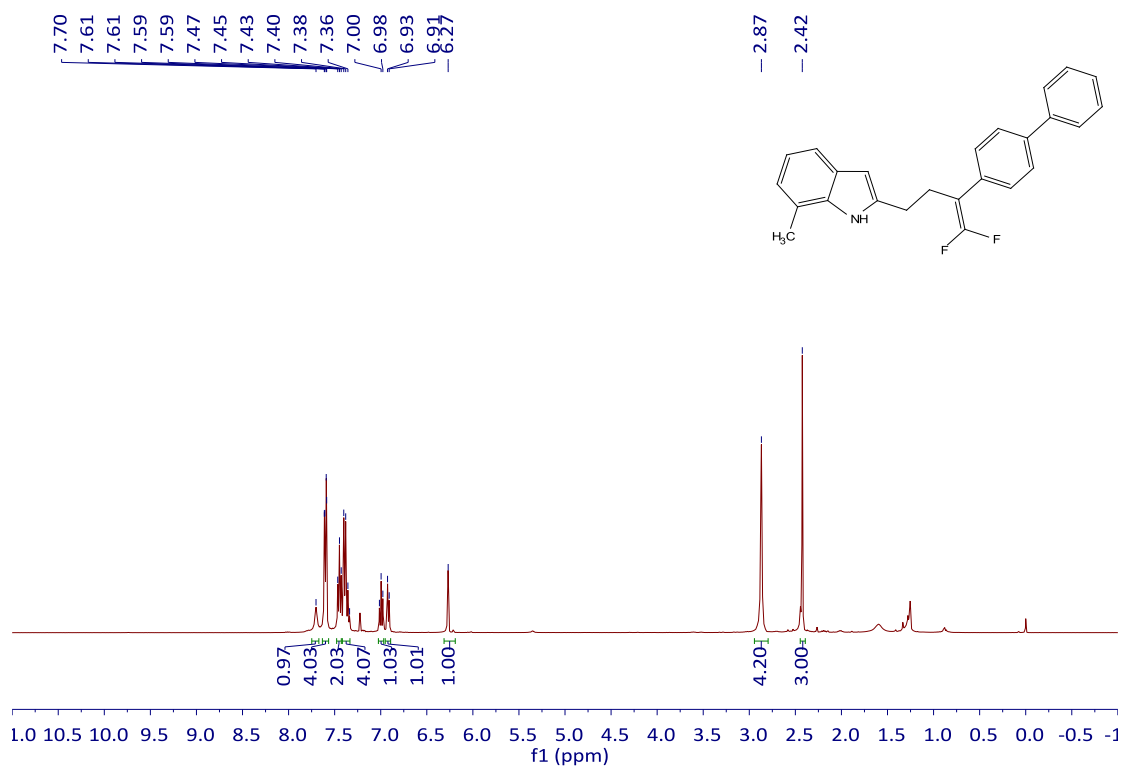
¹H NMR of **3w** (400 Hz, CDCl₃)



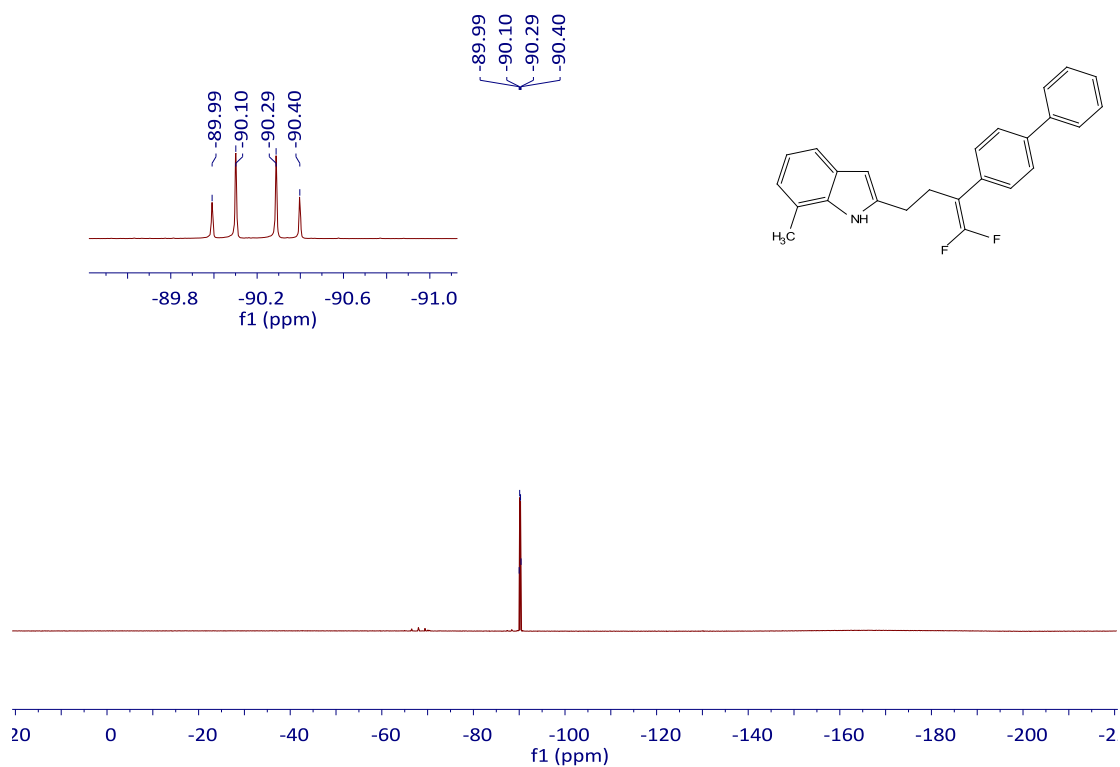
¹⁹F NMR of **3w** (376 Hz, CDCl₃)



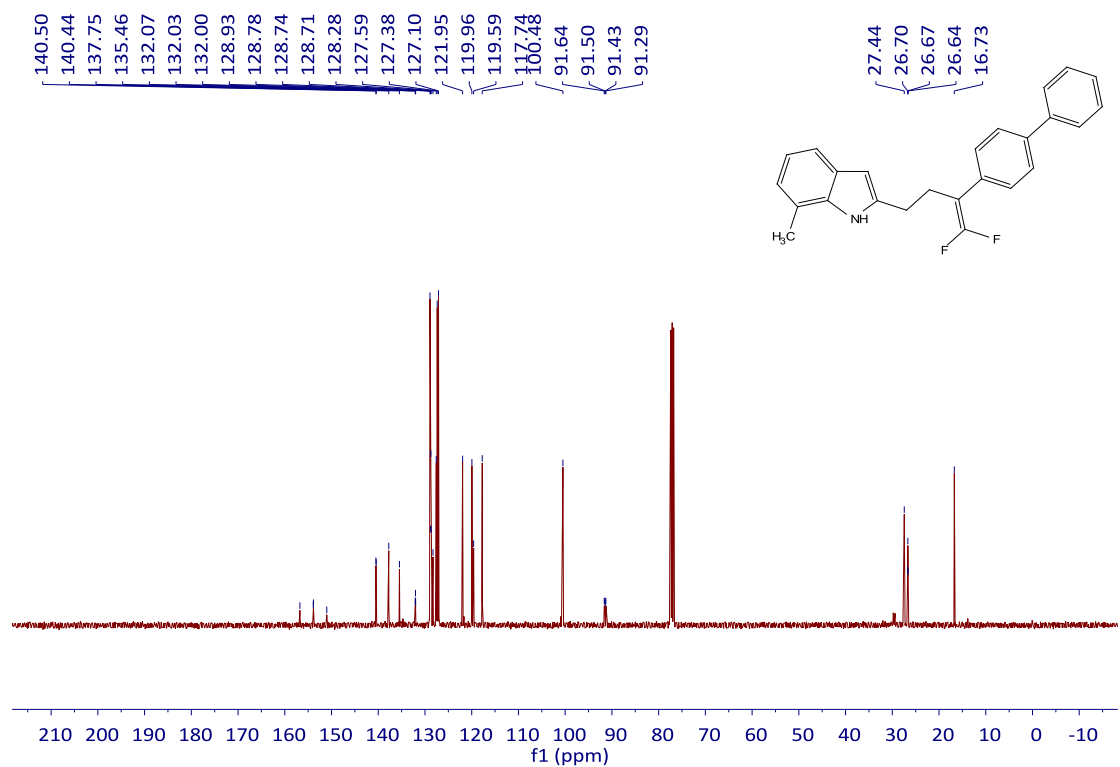
$^{13}\text{C}\{^1\text{H}\}$ NMR of **3w** (100 Hz, CDCl_3)



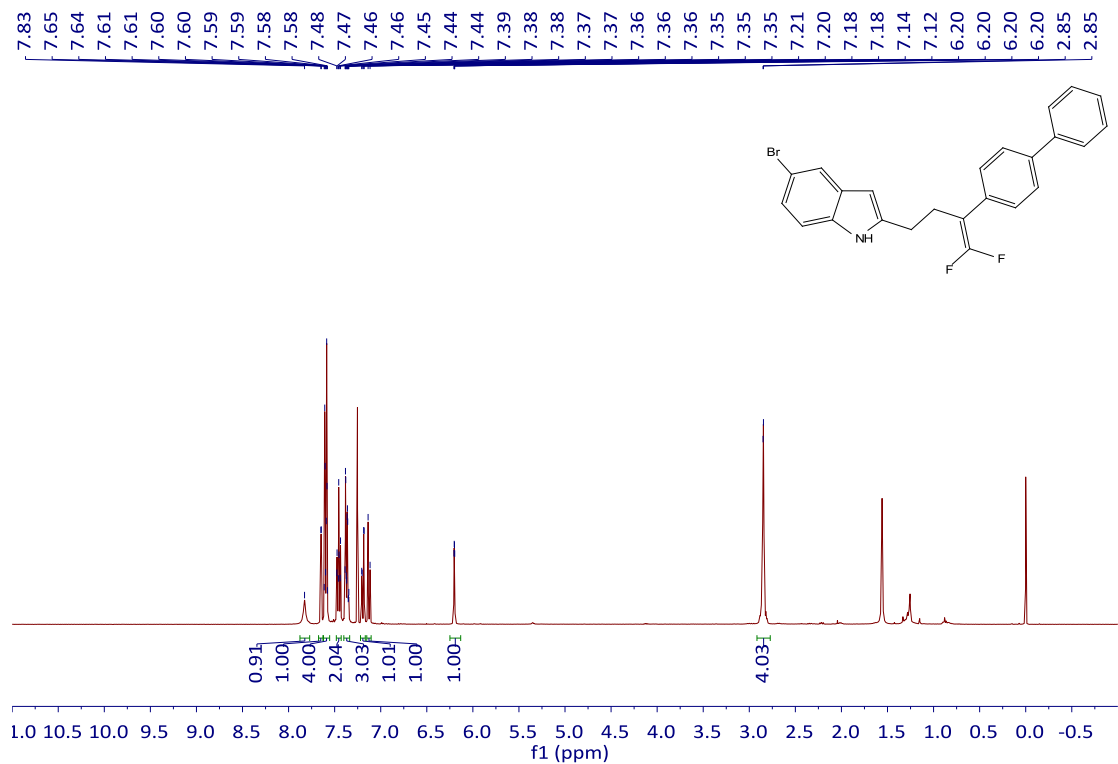
^1H NMR of **3x** (400 Hz, CDCl_3)



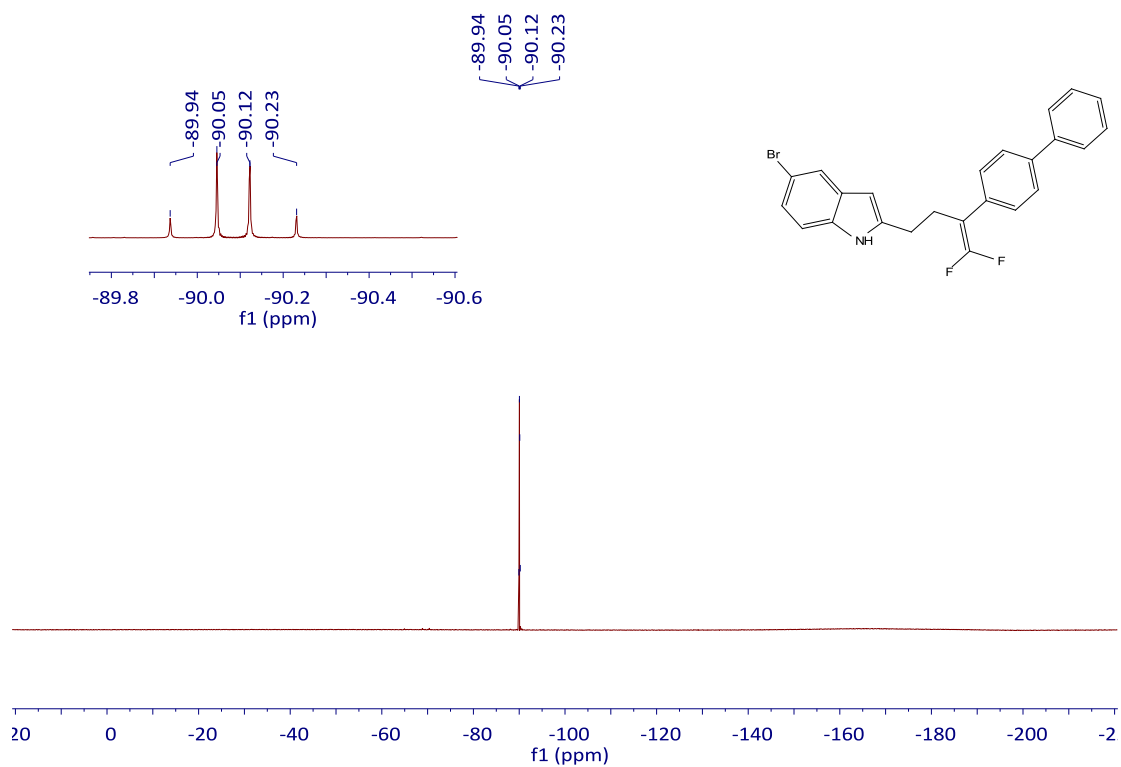
^{19}F NMR of **3x** (376 Hz, CDCl_3)



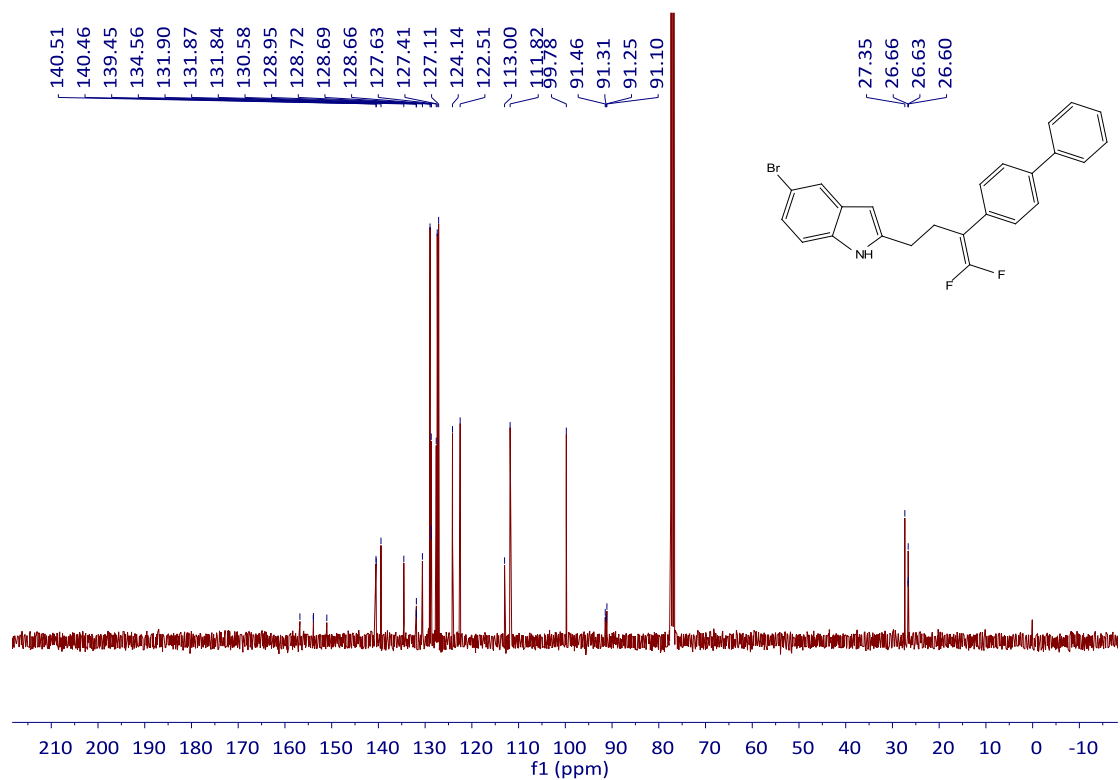
$^{13}\text{C}\{^1\text{H}\}$ NMR of **3x** (100 Hz, CDCl_3)



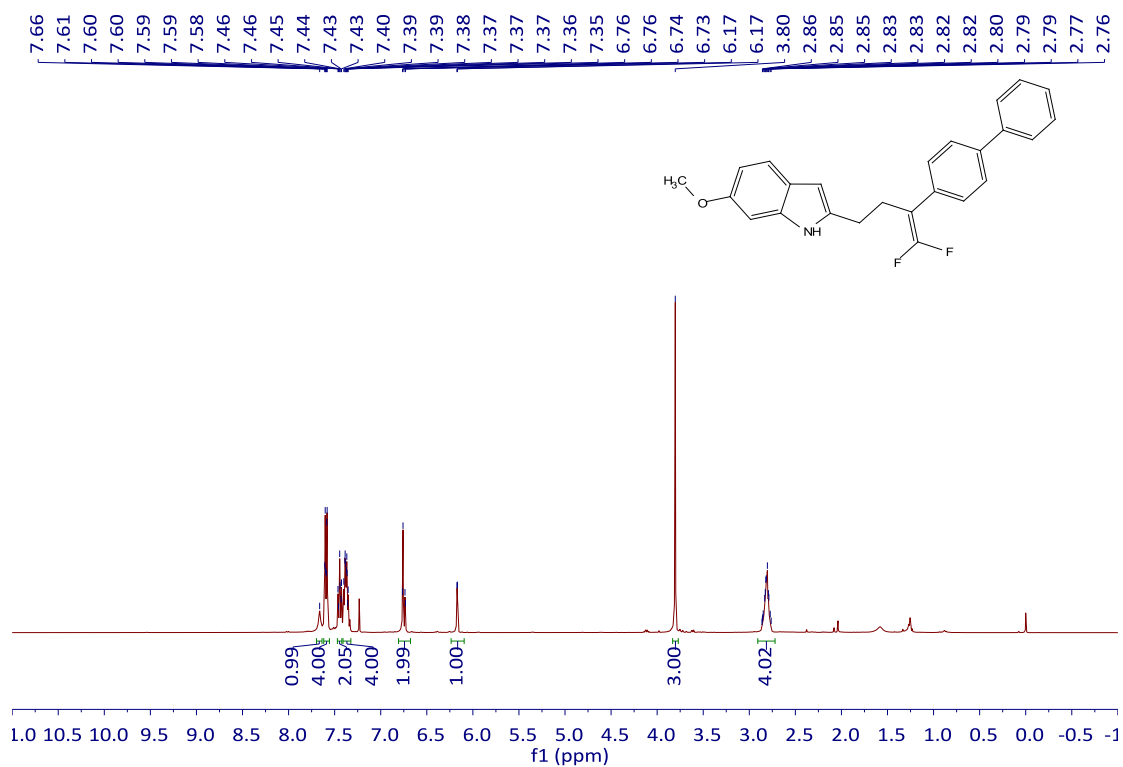
¹H NMR of **3y** (400 Hz, CDCl₃)



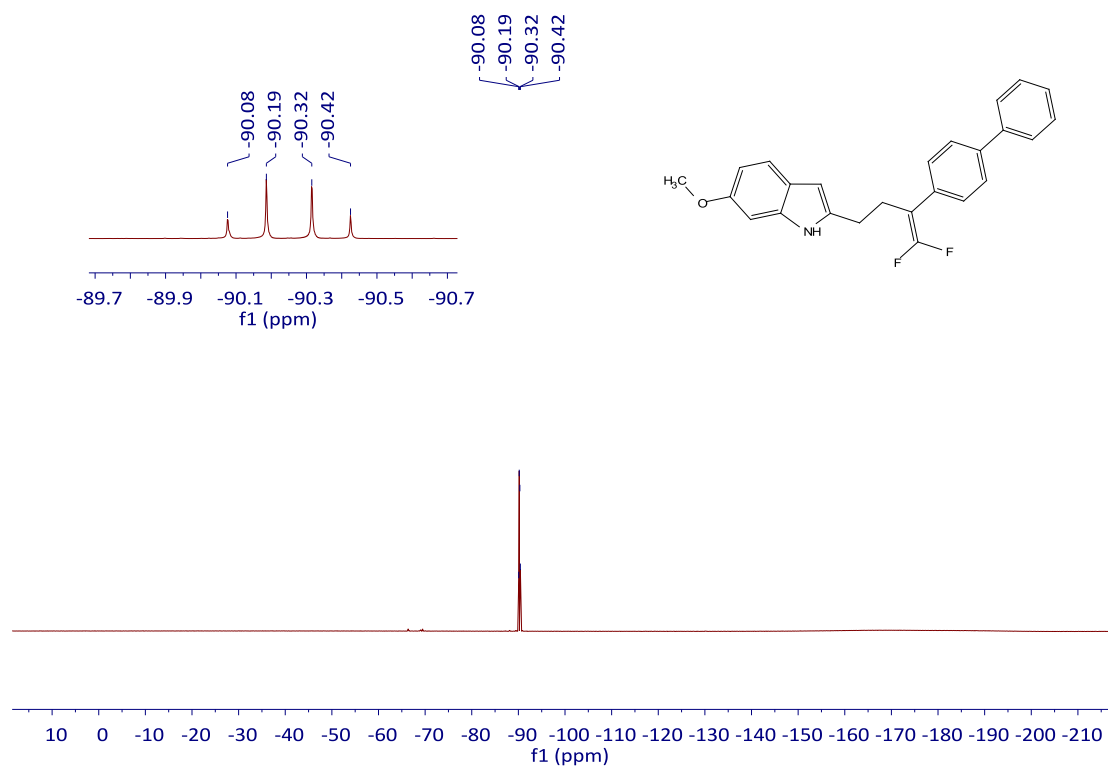
¹⁹F NMR of **3y** (376 Hz, CDCl₃)



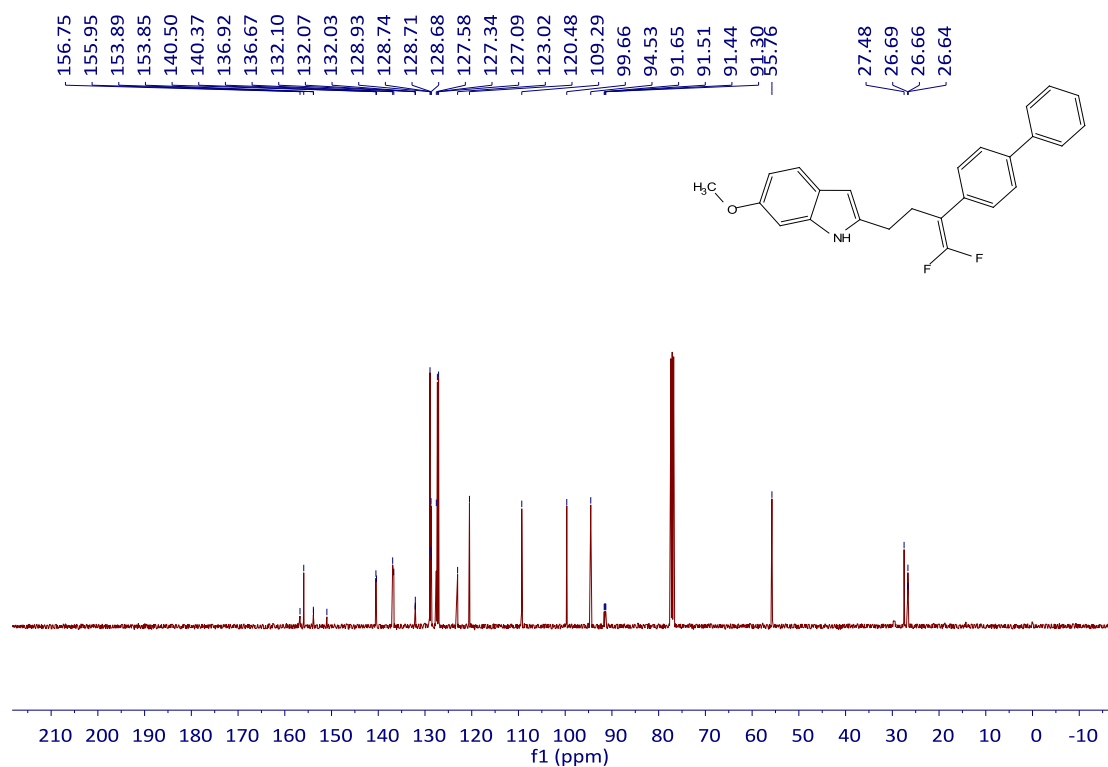
¹³C{¹H} NMR of **3y** (100 Hz, CDCl₃)



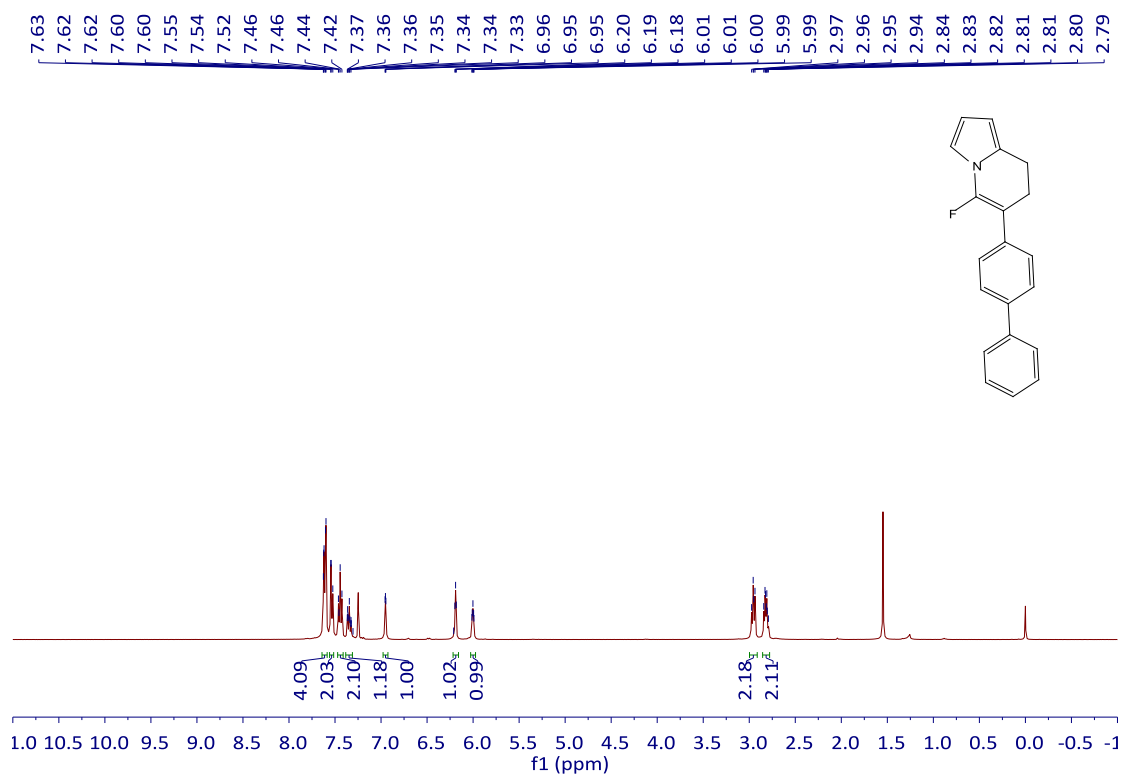
¹H NMR of **3z** (400 Hz, CDCl₃)



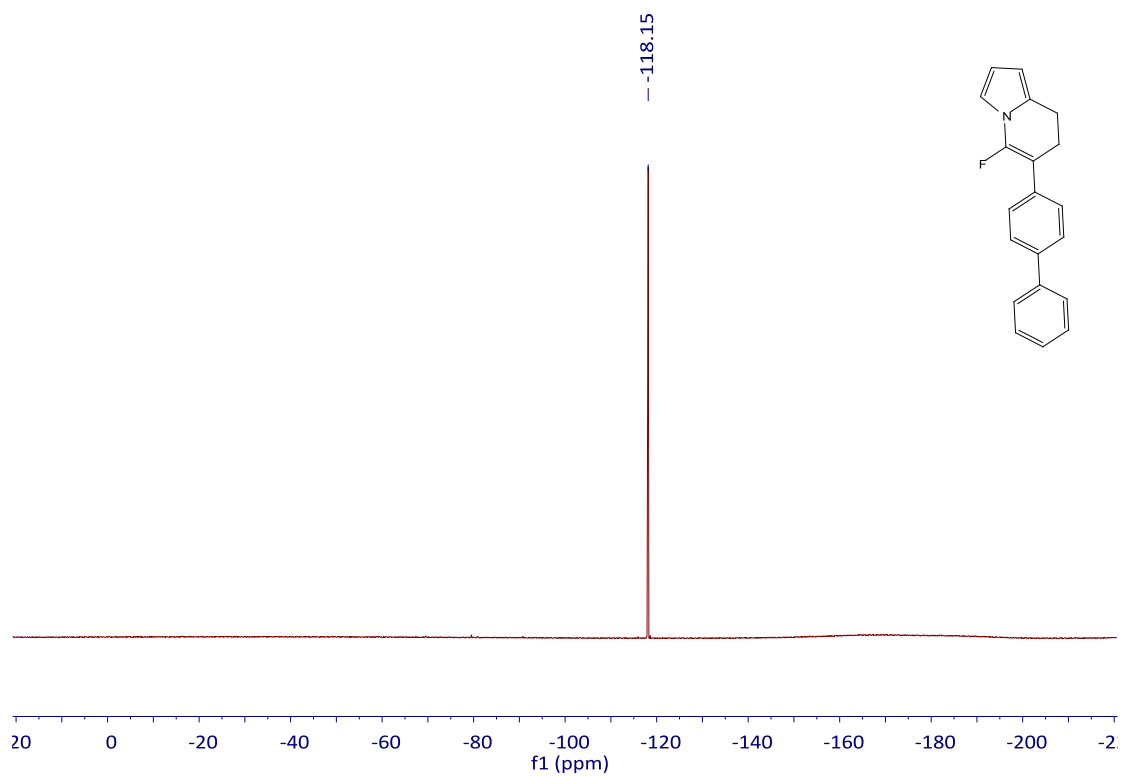
¹⁹F NMR of **3z** (376 Hz, CDCl₃)



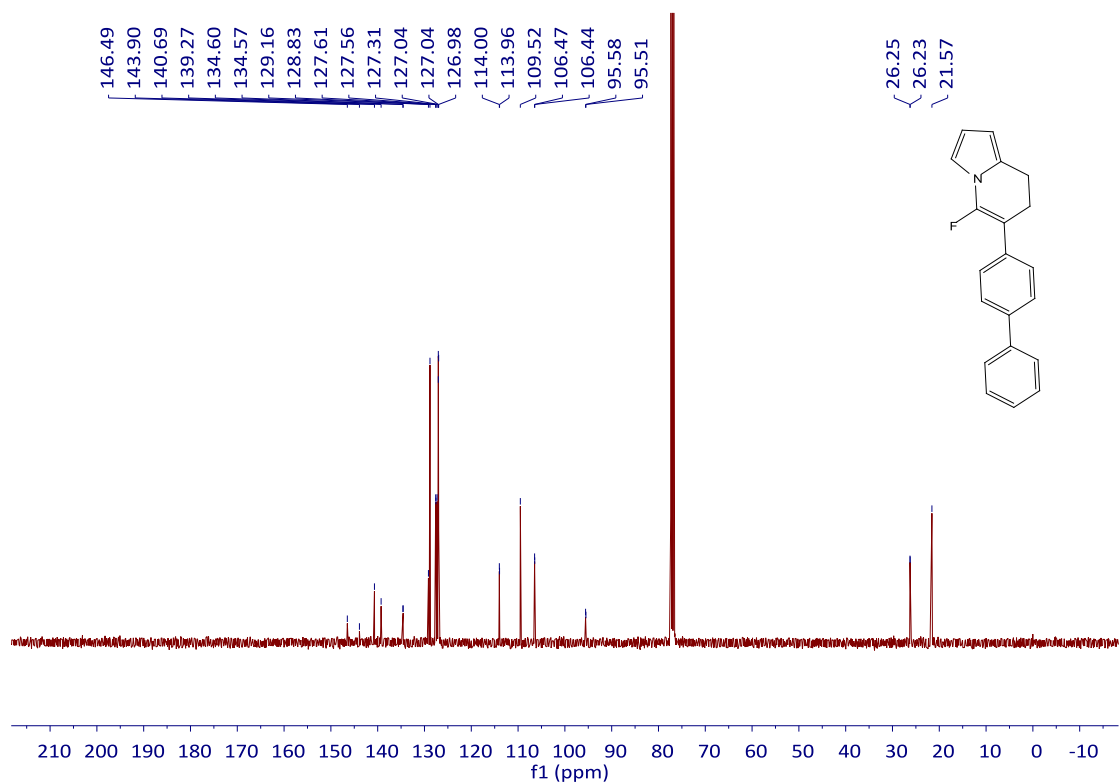
¹³C{¹H} NMR of **3z** (100 Hz, CDCl₃)



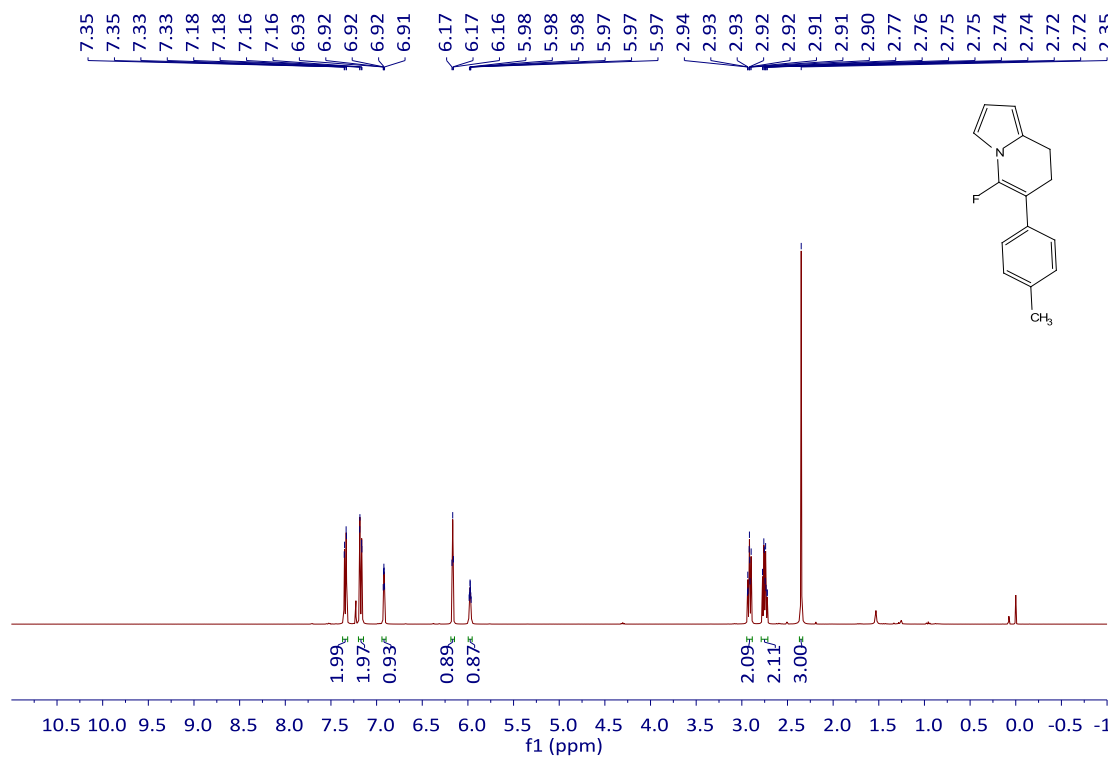
¹H NMR of **4a** (400 Hz, CDCl₃)



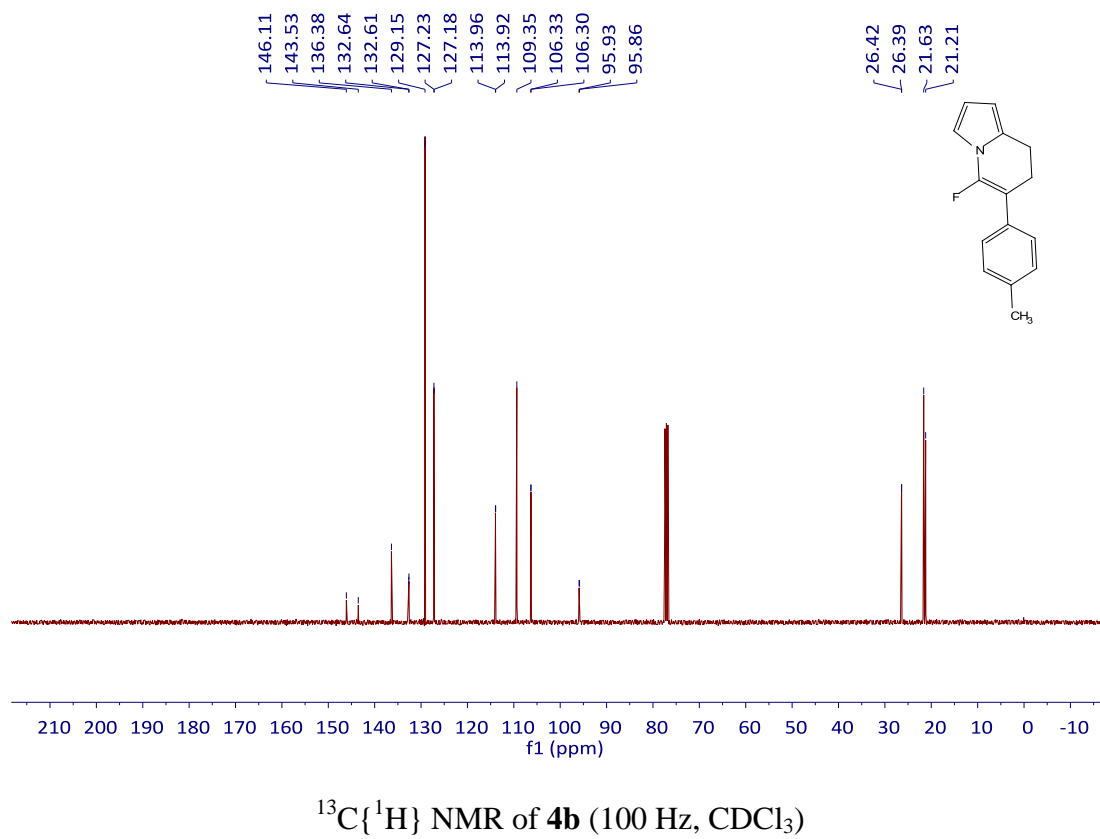
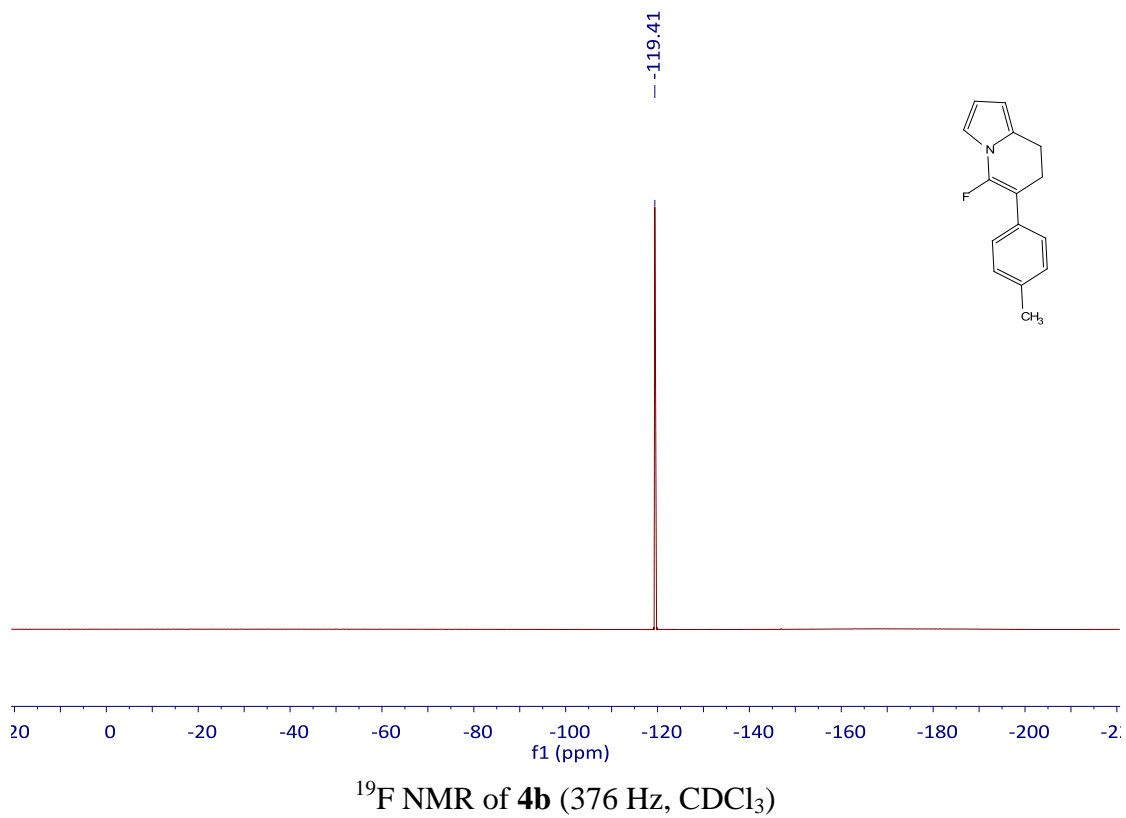
¹⁹F NMR of **4a** (376 Hz, CDCl₃)

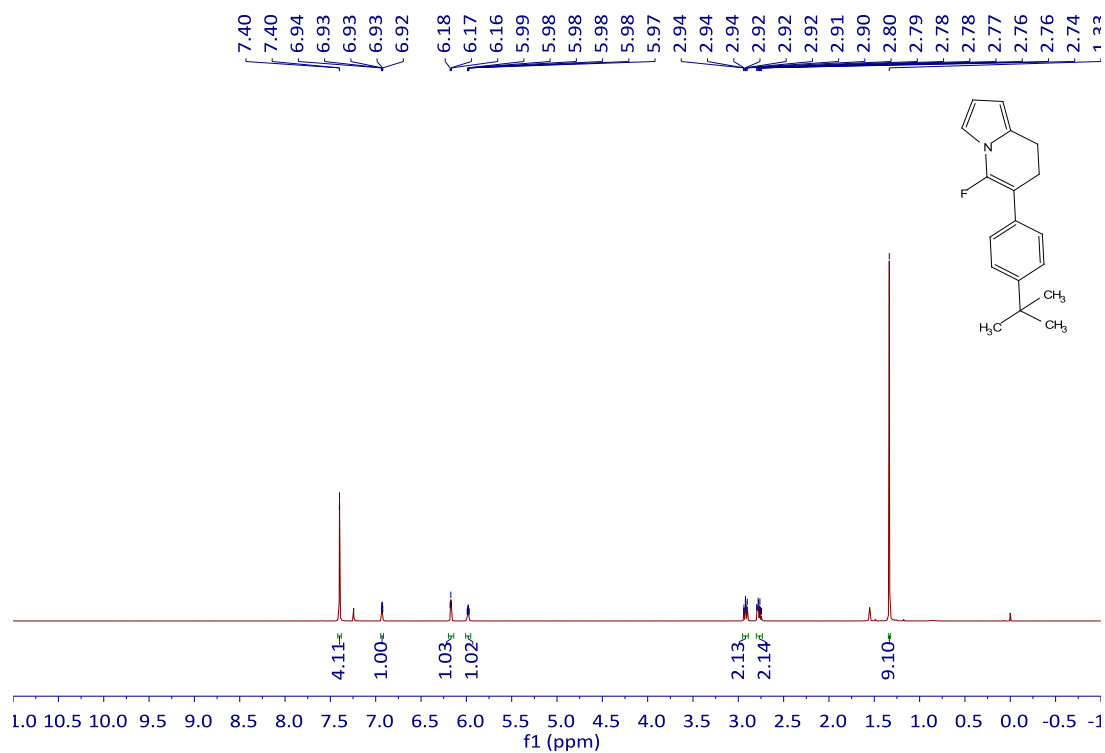


$^{13}\text{C}\{^1\text{H}\}$ NMR of **4a** (100 Hz, CDCl_3)

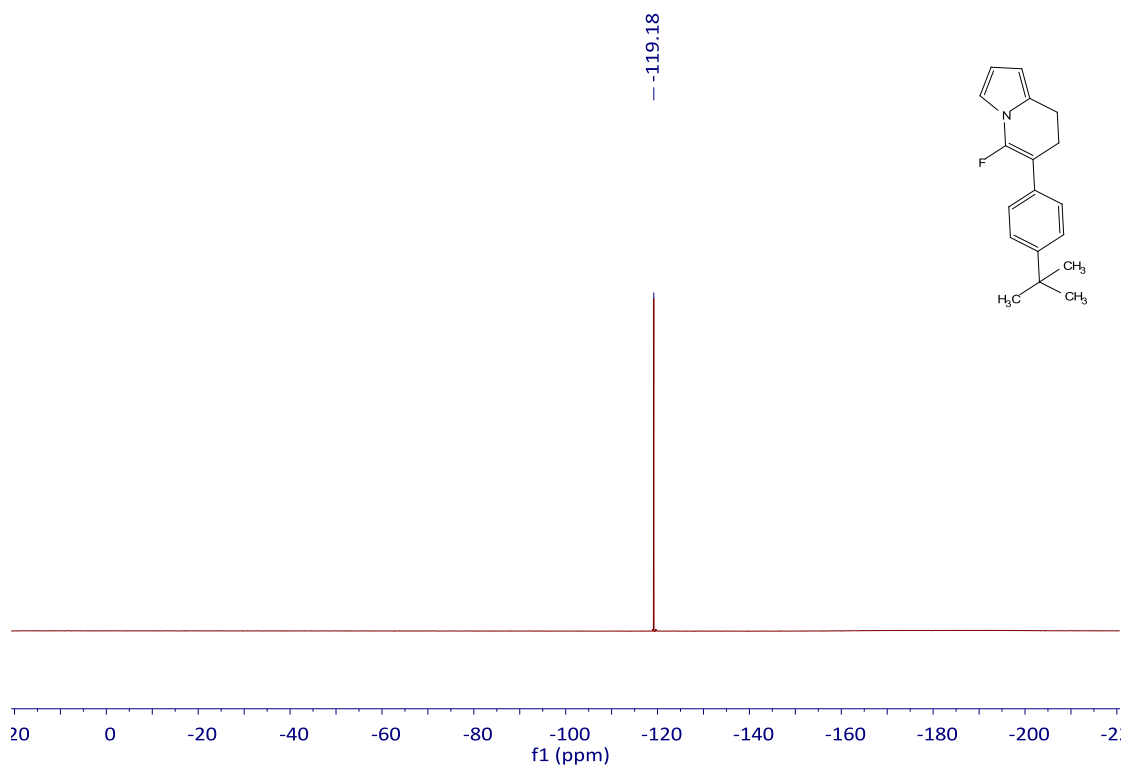


^1H NMR of **4b** (400 Hz, CDCl_3)

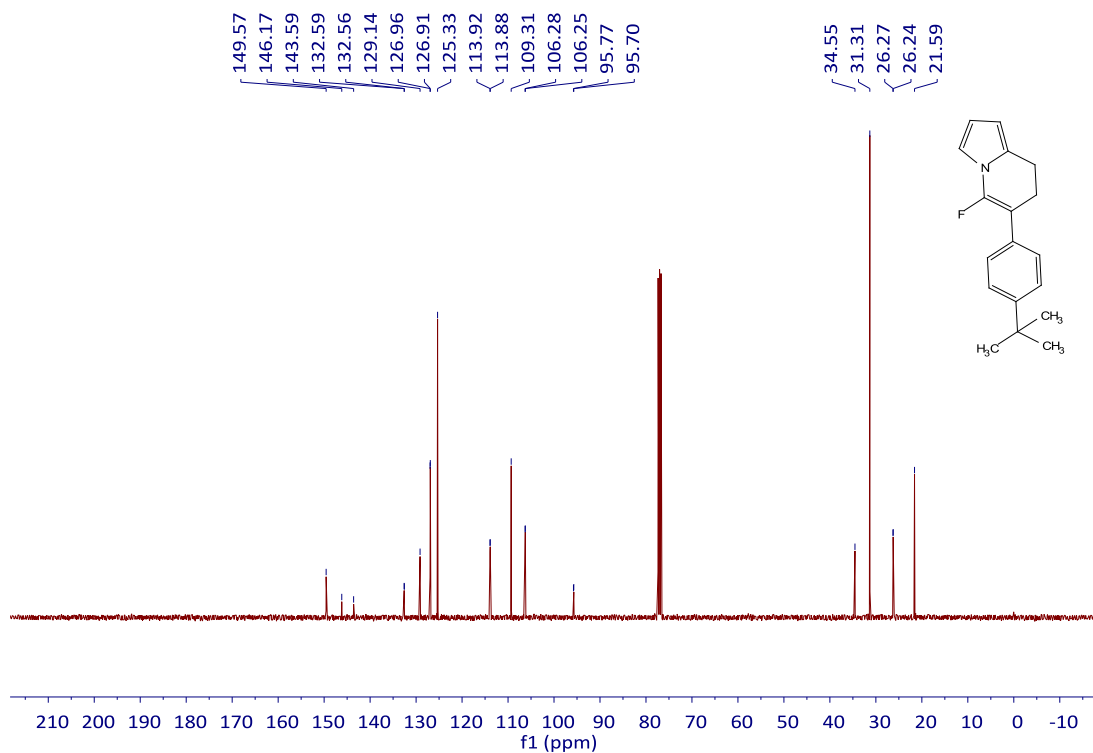




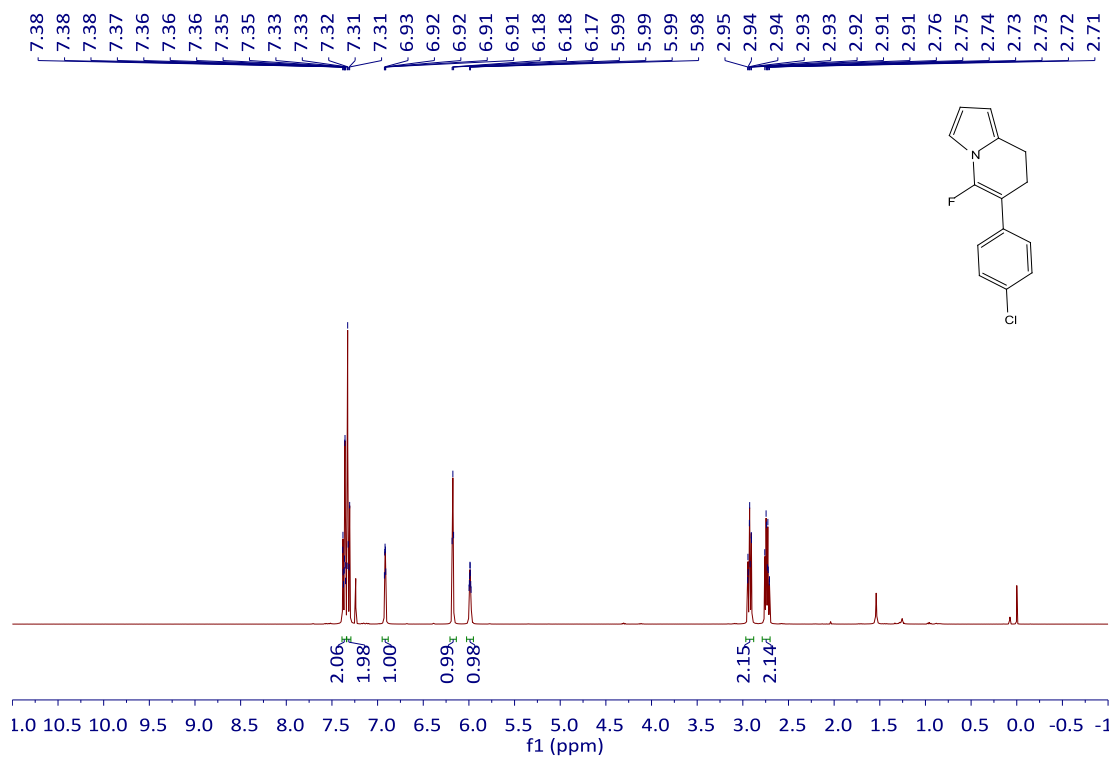
¹H NMR of **4c** (400 Hz, CDCl₃)



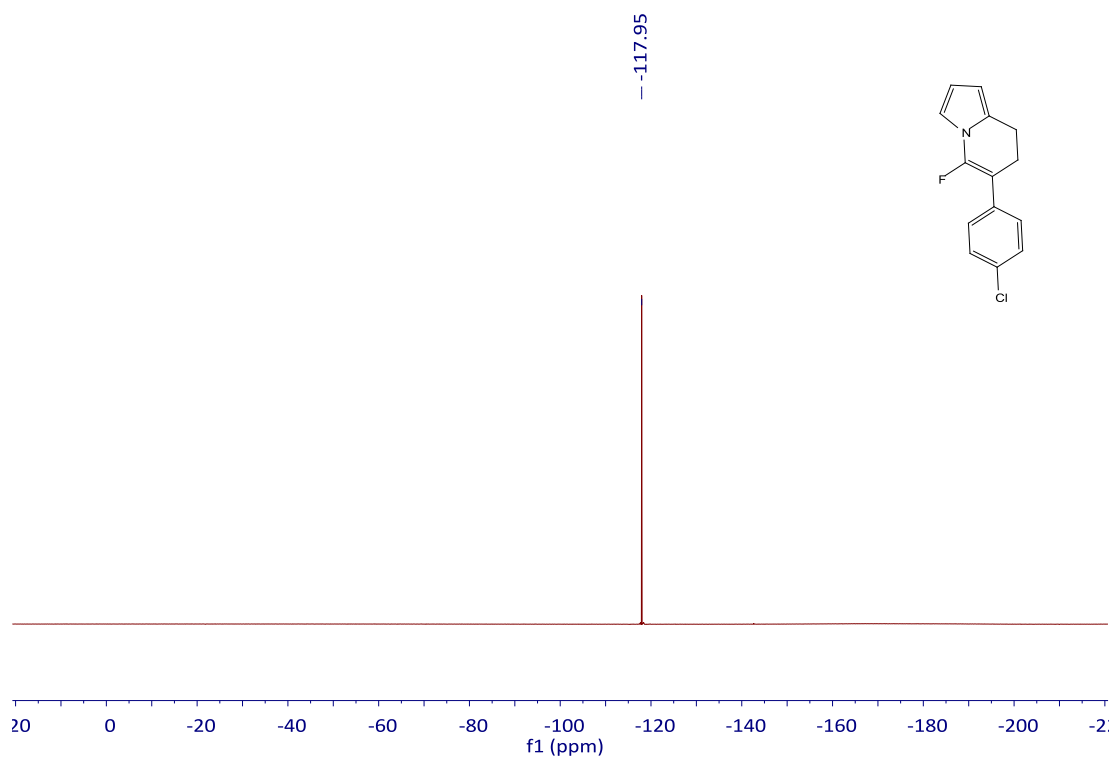
¹⁹F NMR of **4c** (376 Hz, CDCl₃)



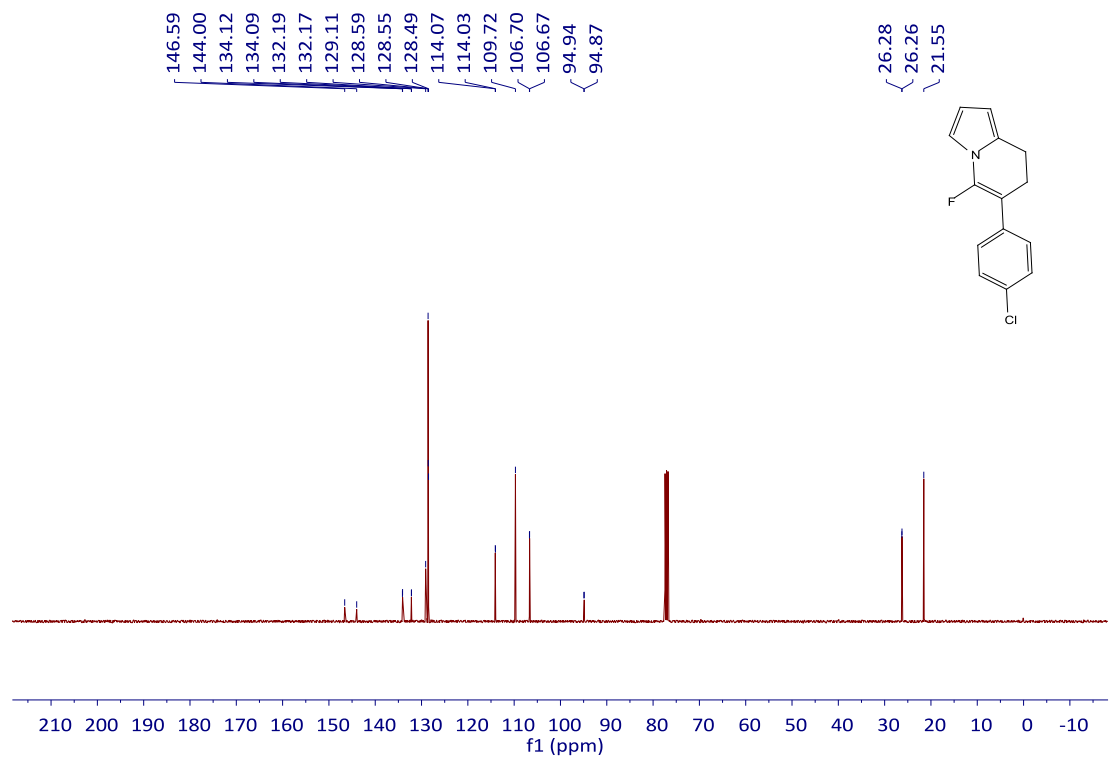
$^{13}\text{C}\{^1\text{H}\}$ NMR of **4c** (100 Hz, CDCl_3)



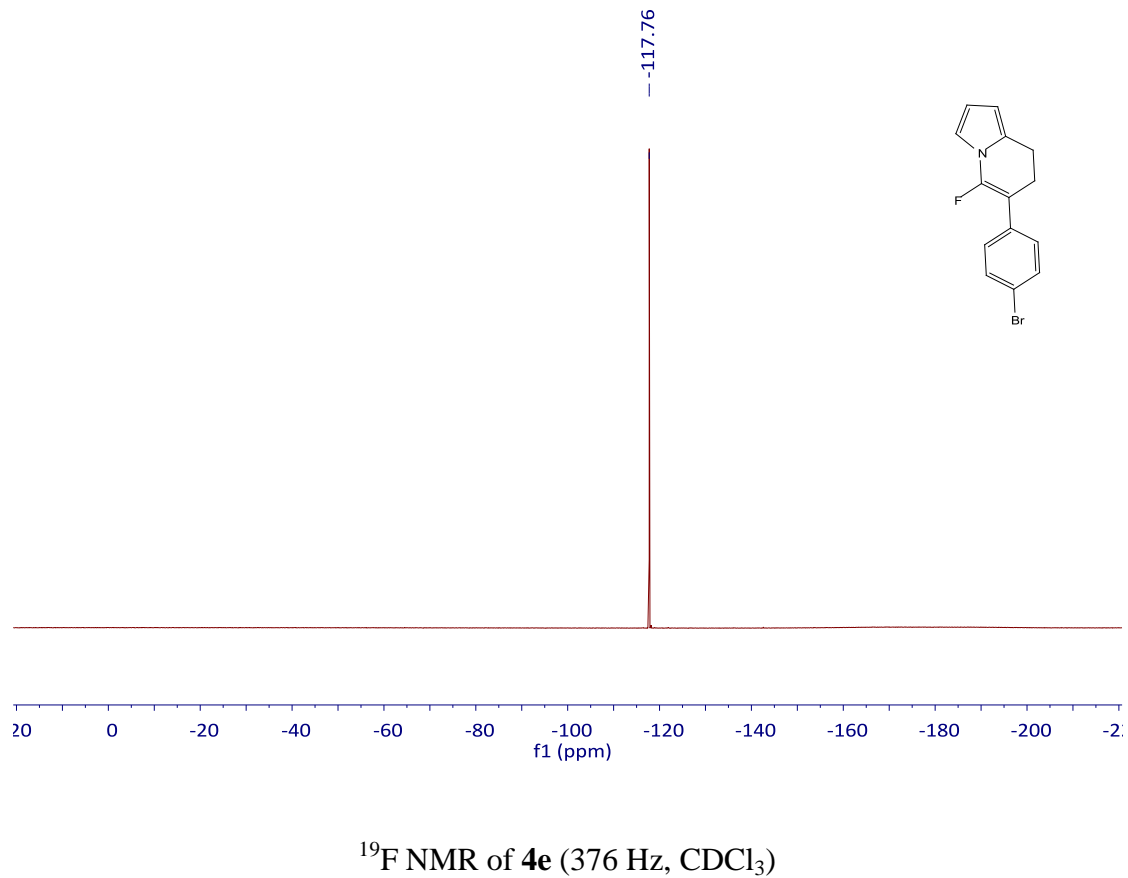
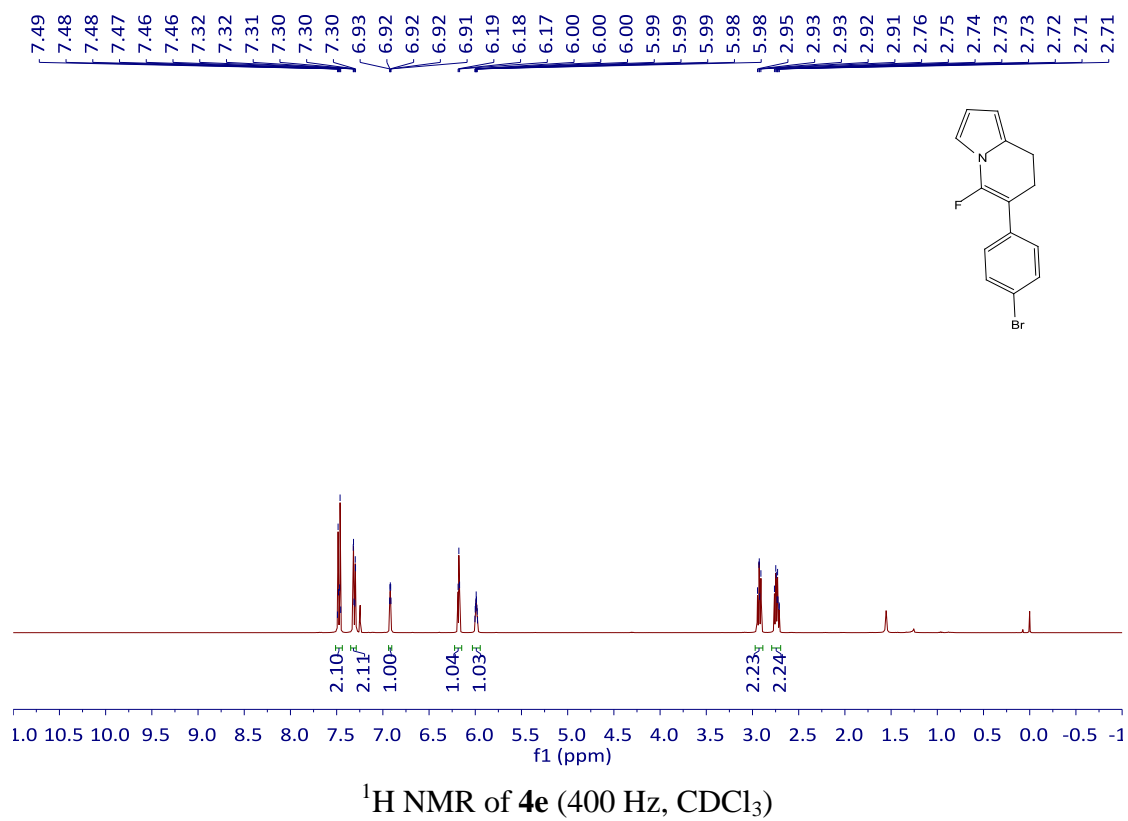
^1H NMR of **4d** (400 Hz, CDCl_3)

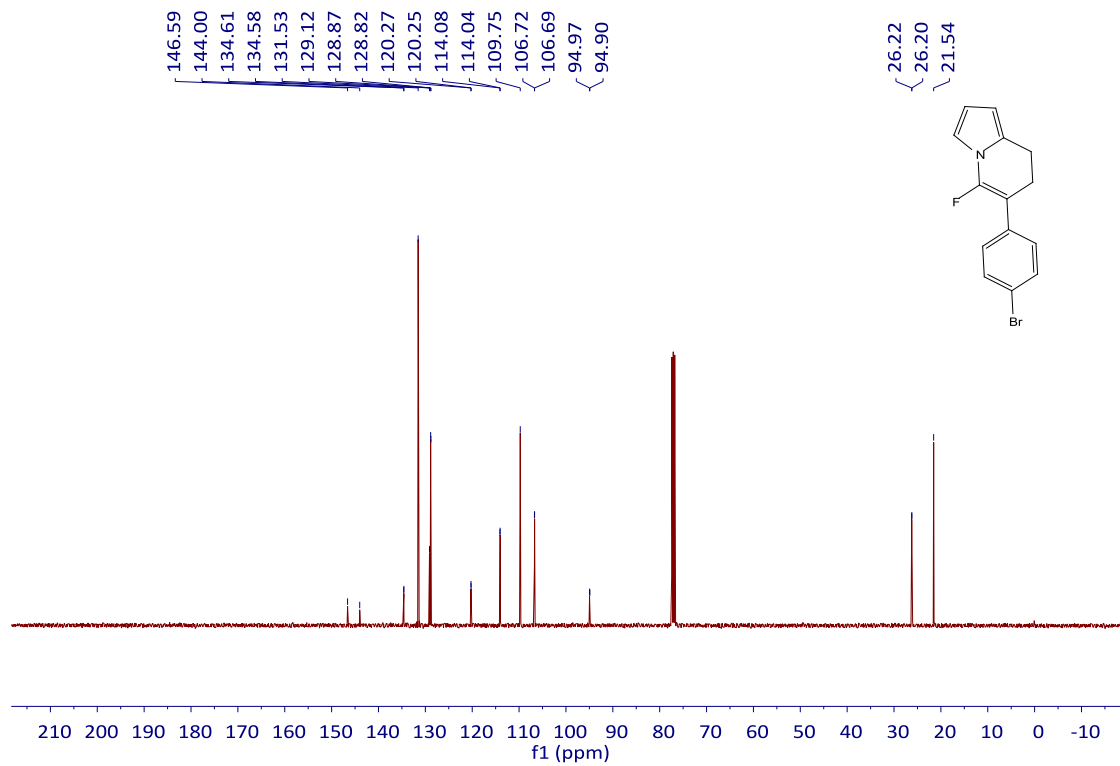


^{19}F NMR of **4d** (376 Hz, CDCl_3)

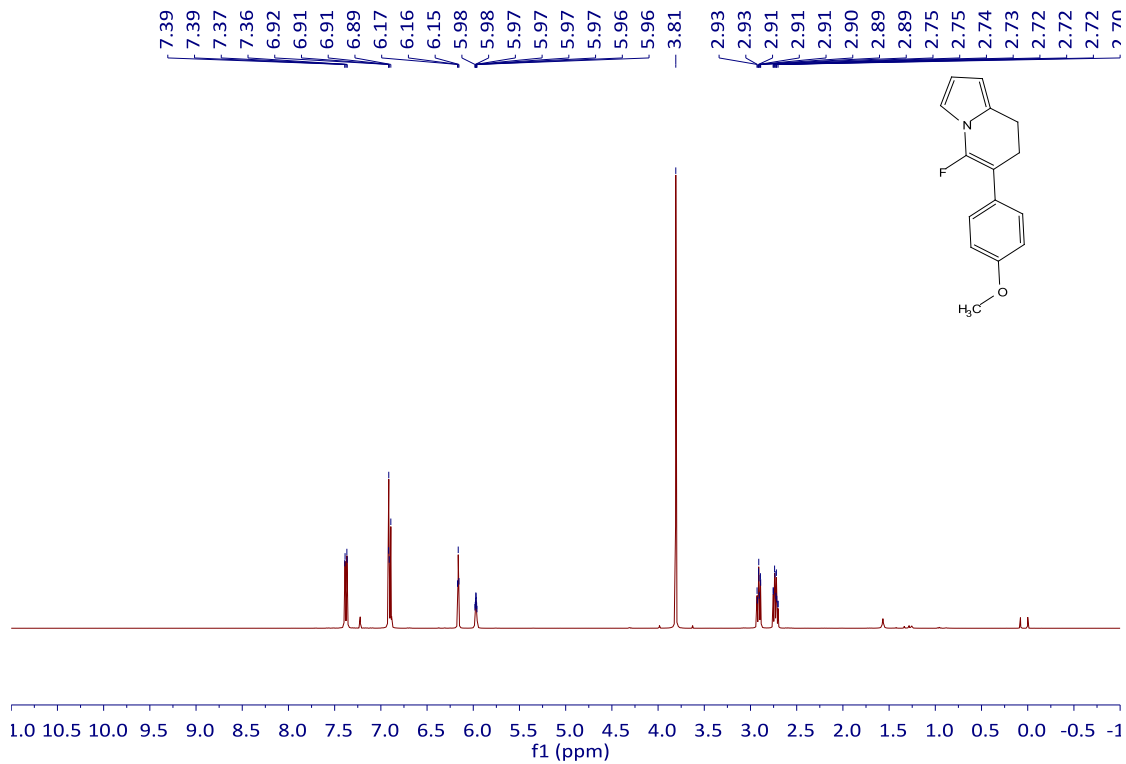


$^{13}\text{C}\{^1\text{H}\}$ NMR of **4d** (100 Hz, CDCl_3)

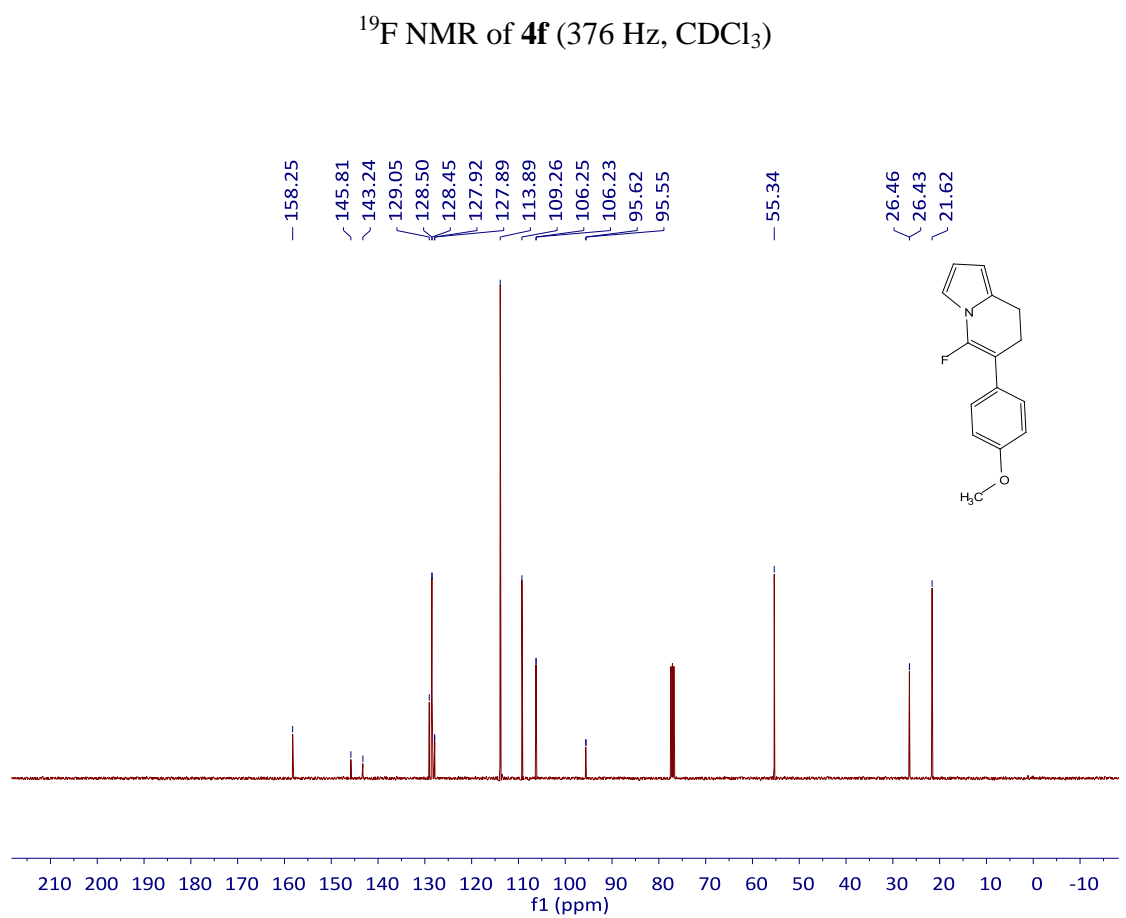
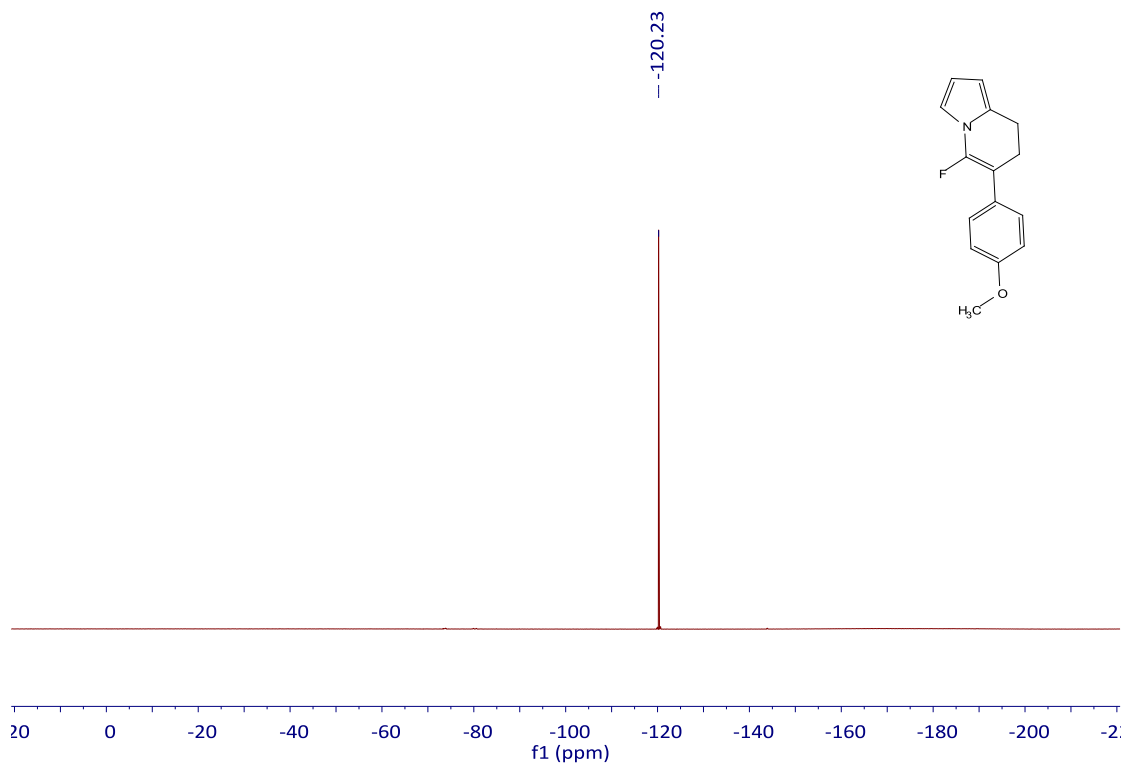




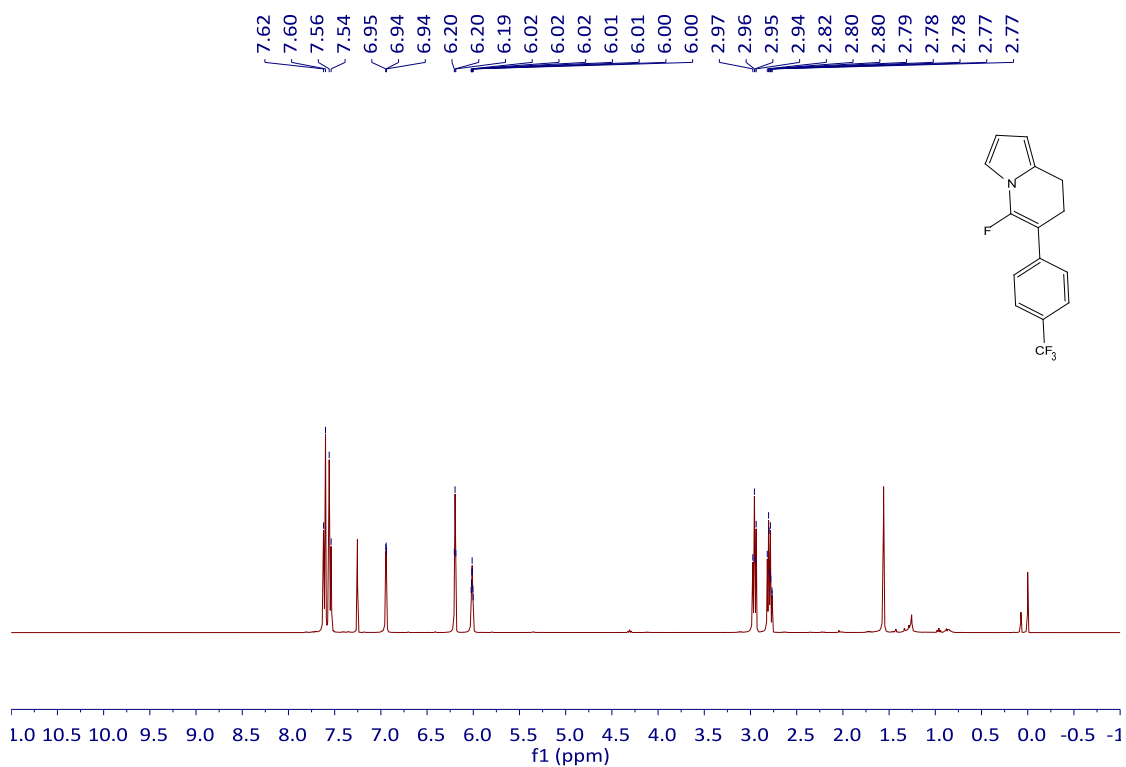
$^{13}\text{C}\{^1\text{H}\}$ NMR of **4e** (100 Hz, CDCl_3)



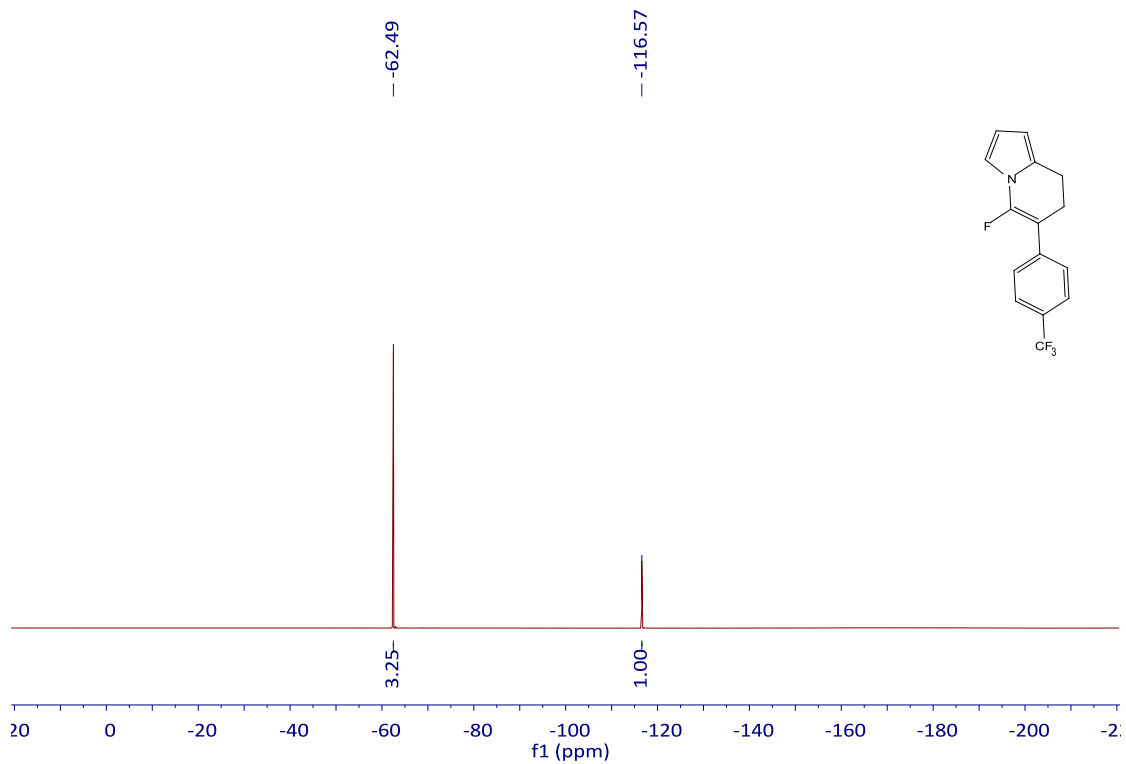
^1H NMR of **4f** (400 Hz, CDCl_3)



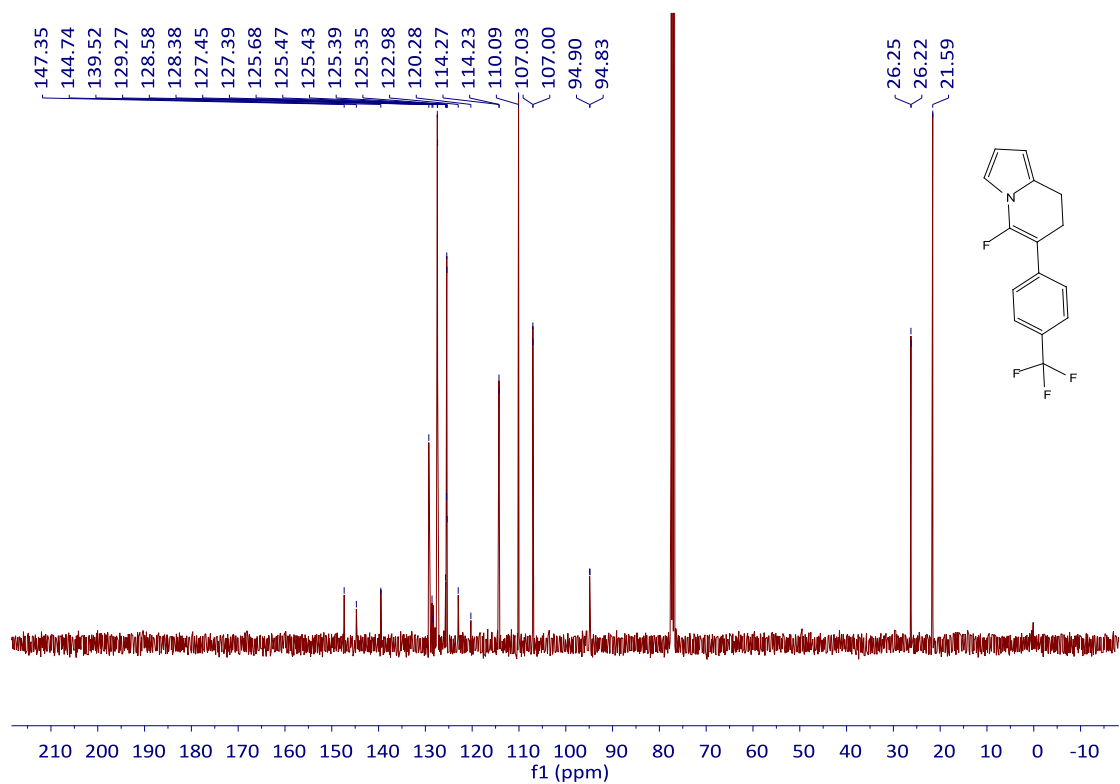
$^{13}\text{C}\{^1\text{H}\}$ NMR of **4f** (100 Hz, CDCl_3)



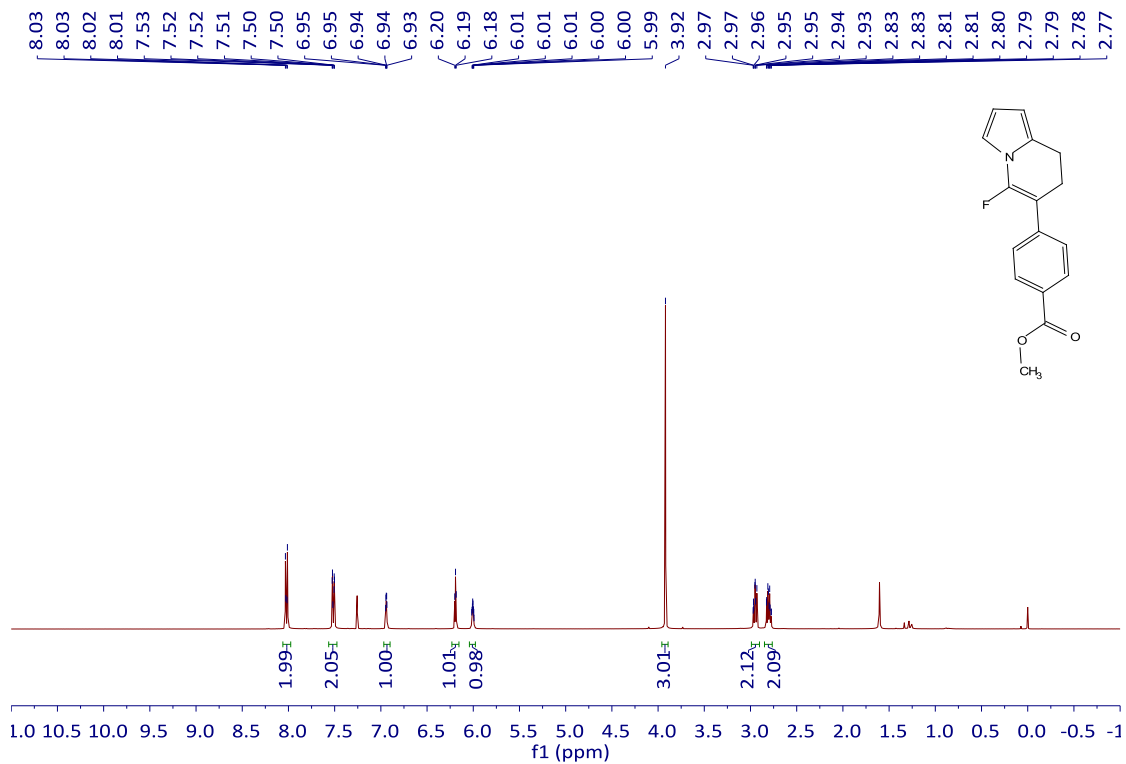
¹H NMR of **4g** (400 Hz, CDCl₃)



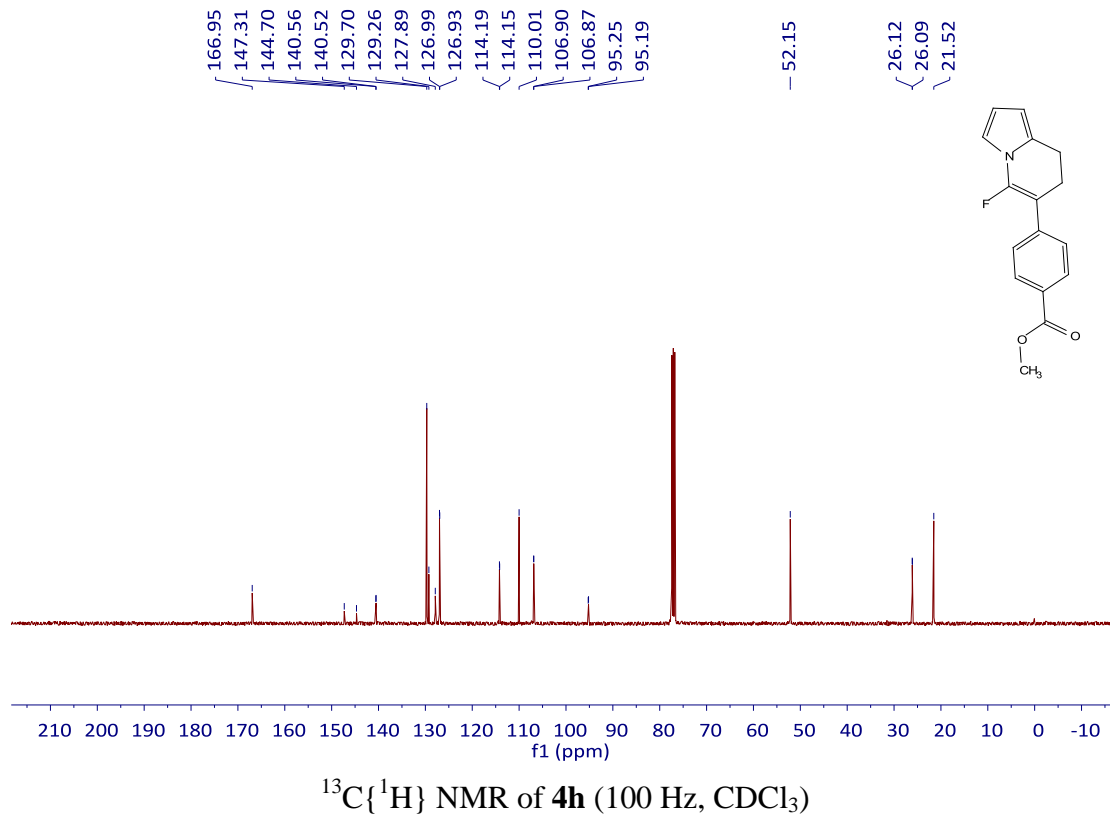
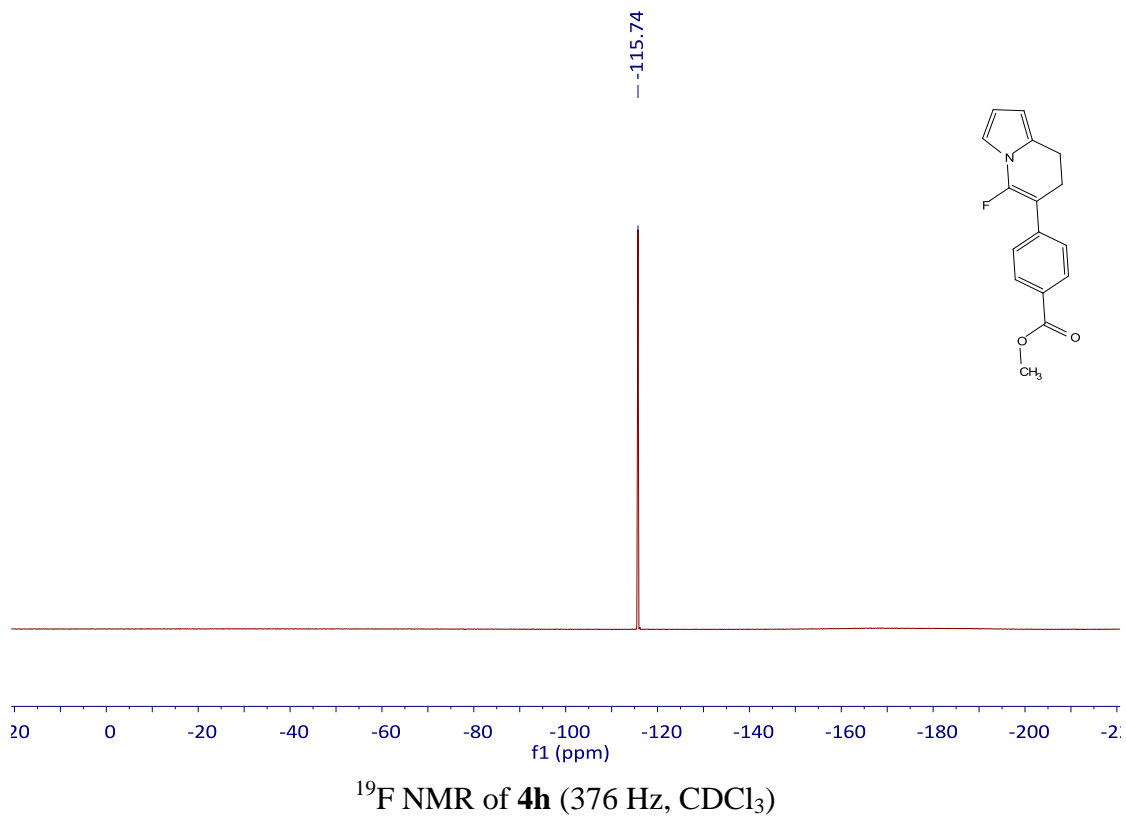
¹⁹F NMR of **4g** (376 Hz, CDCl₃)

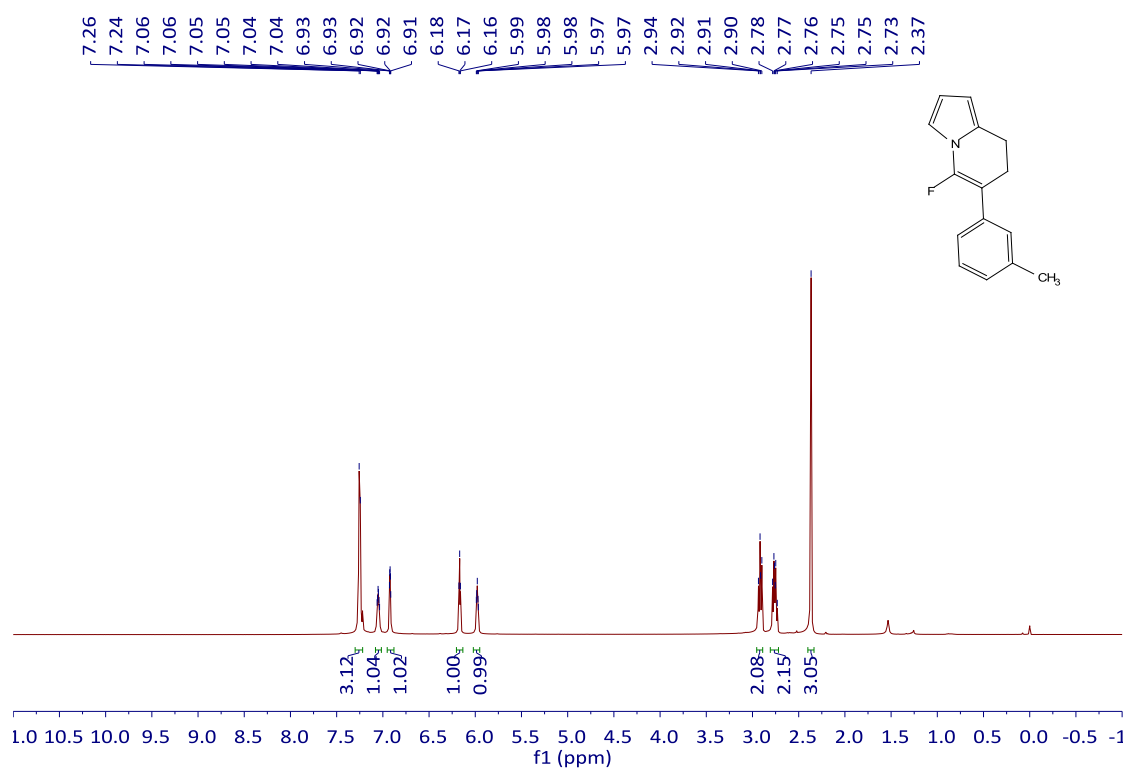


¹³C{¹H} NMR of **4g** (100 Hz, CDCl₃)

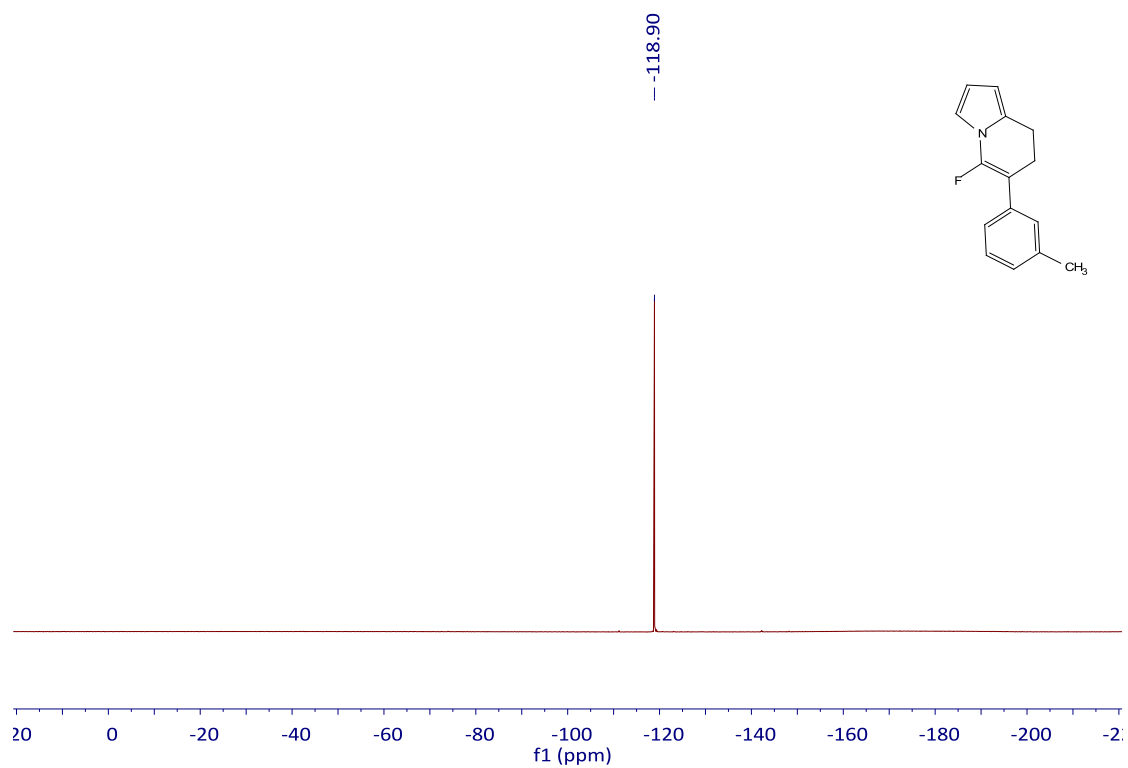


¹H NMR of **4h** (400 Hz, CDCl₃)

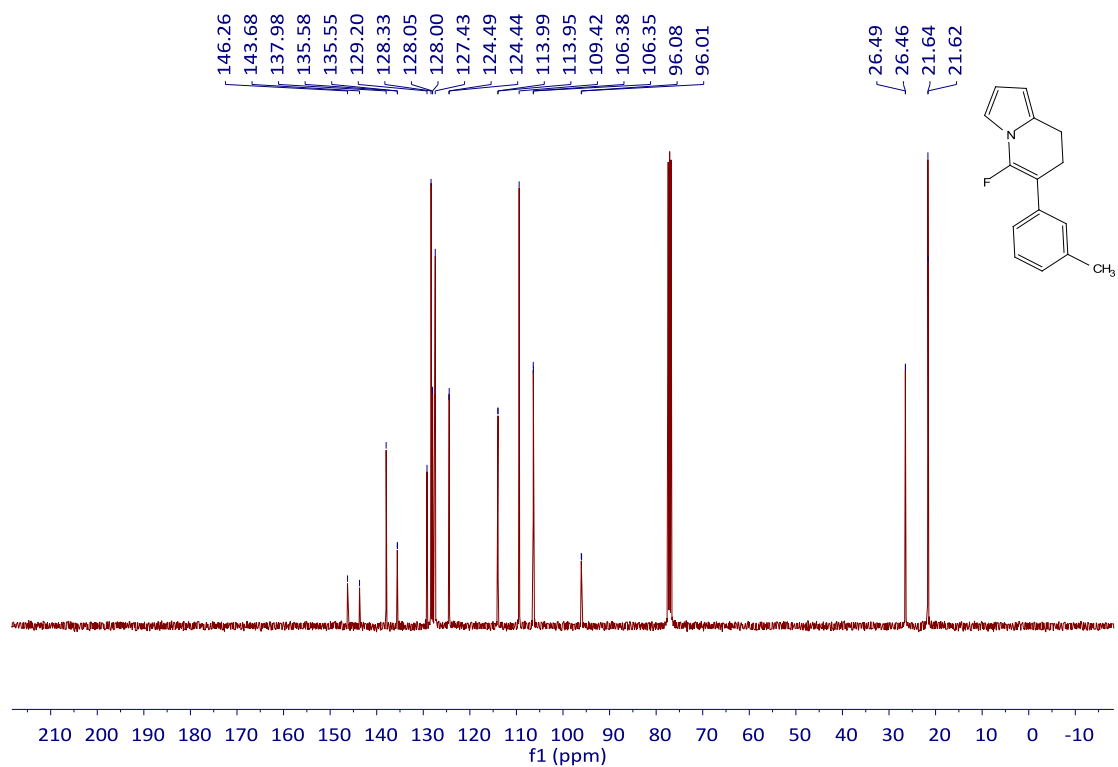




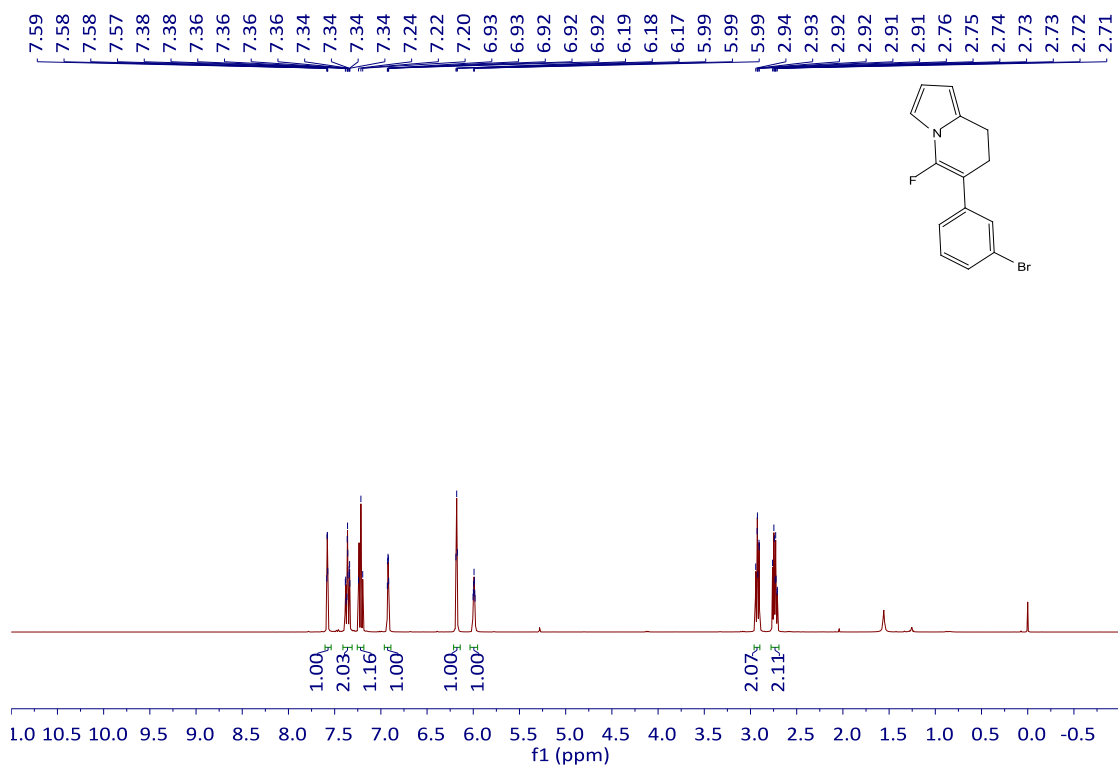
¹H NMR of **4i** (400 Hz, CDCl₃)



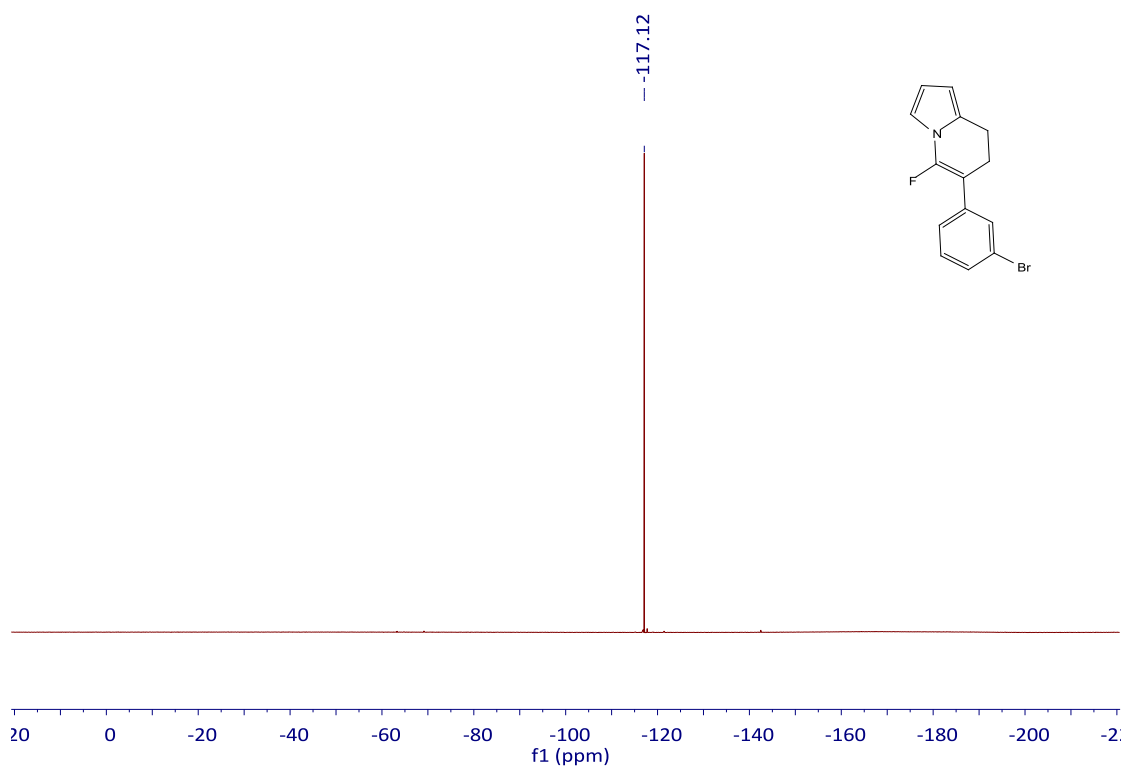
¹⁹F NMR of **4i** (376 Hz, CDCl₃)



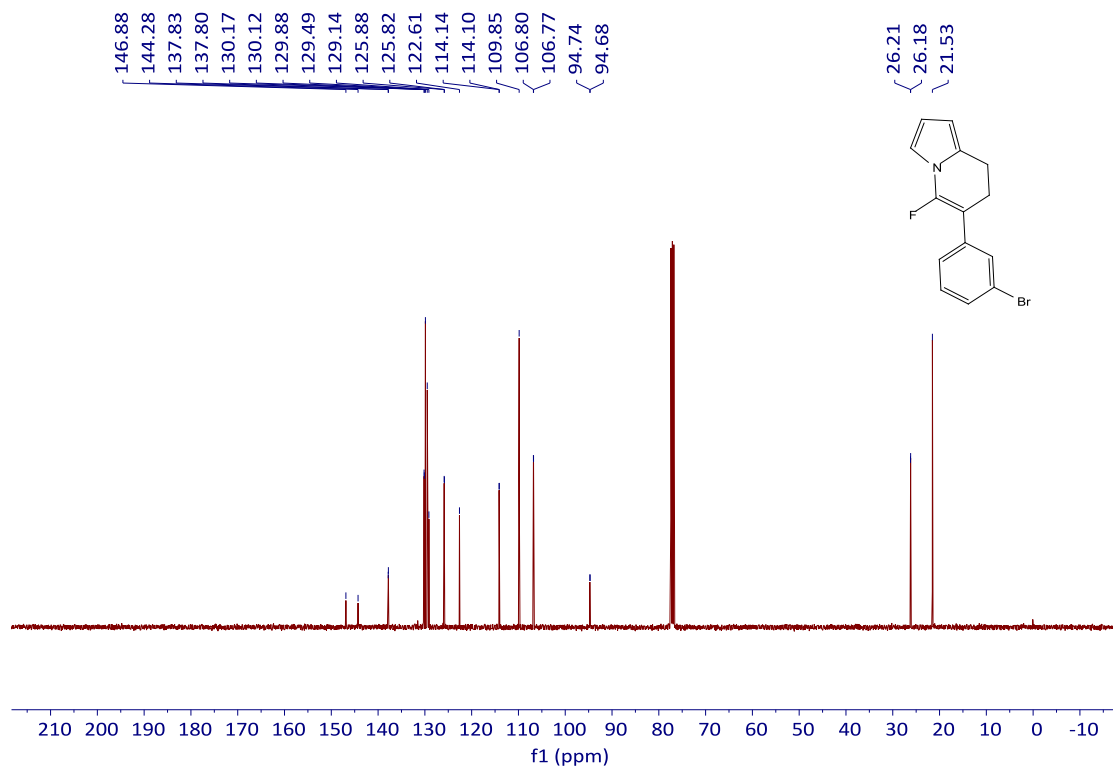
¹³C{¹H} NMR of **4i** (100 Hz, CDCl₃)



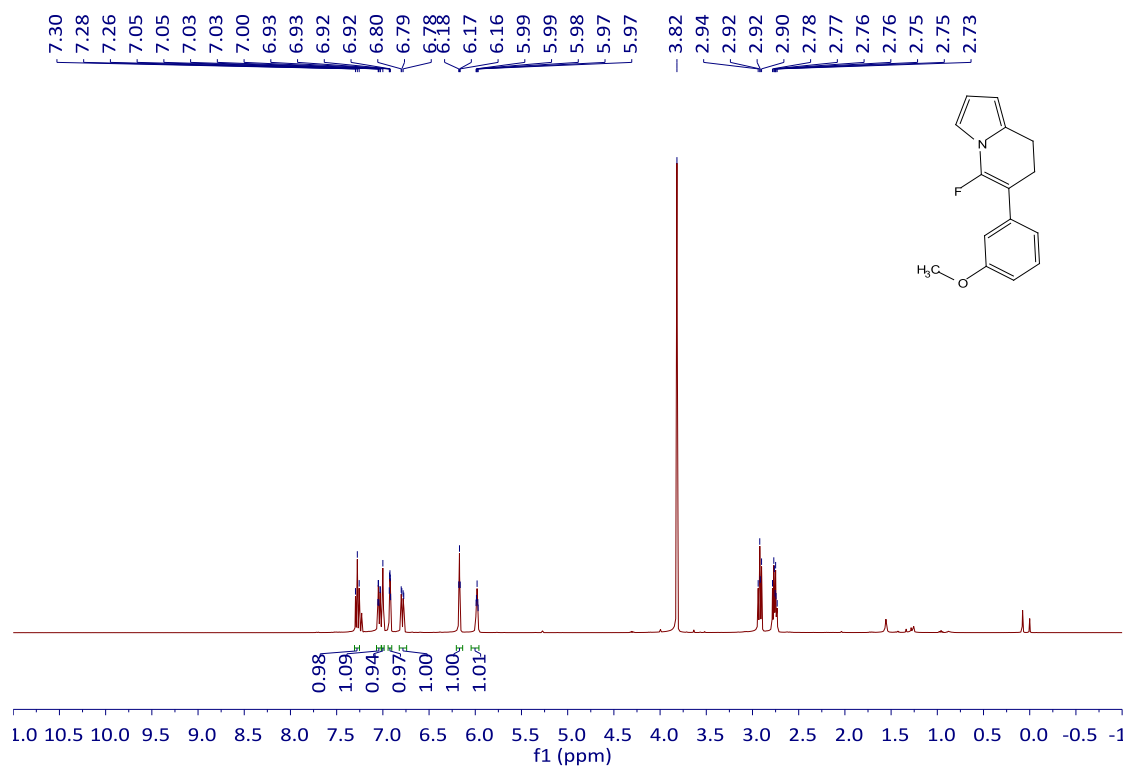
¹H NMR of **4j** (400 Hz, CDCl₃)



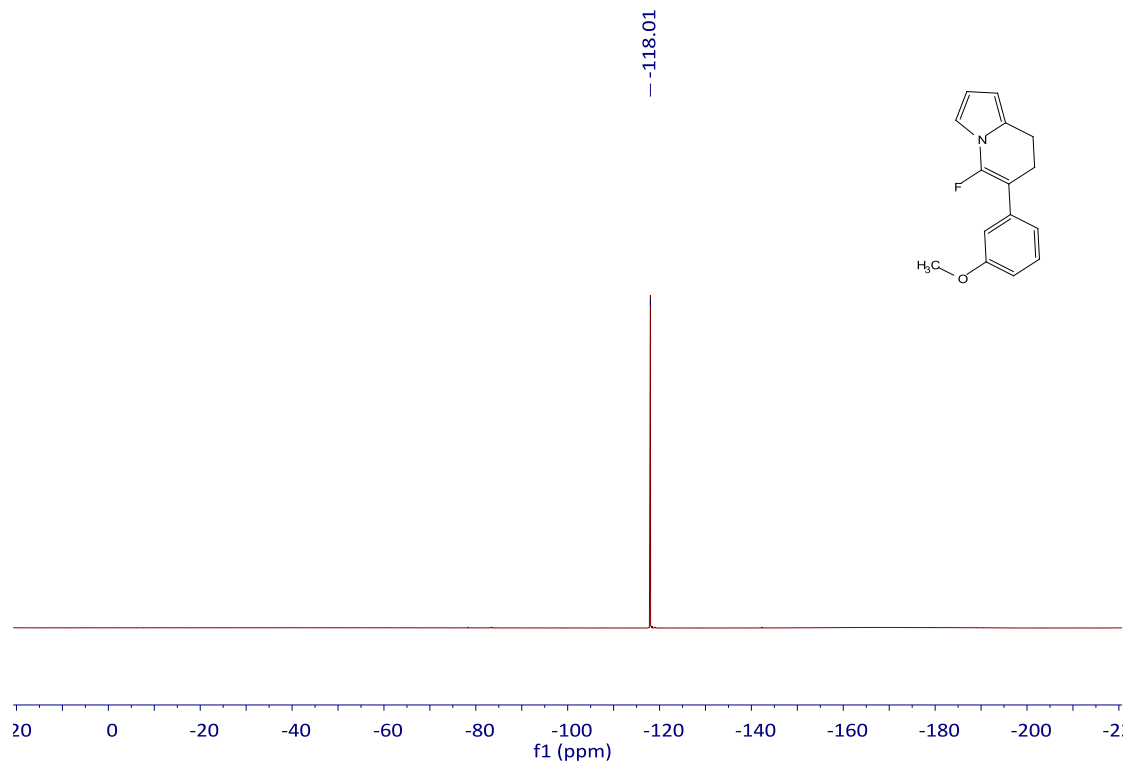
^{19}F NMR of **4j** (376 Hz, CDCl_3)



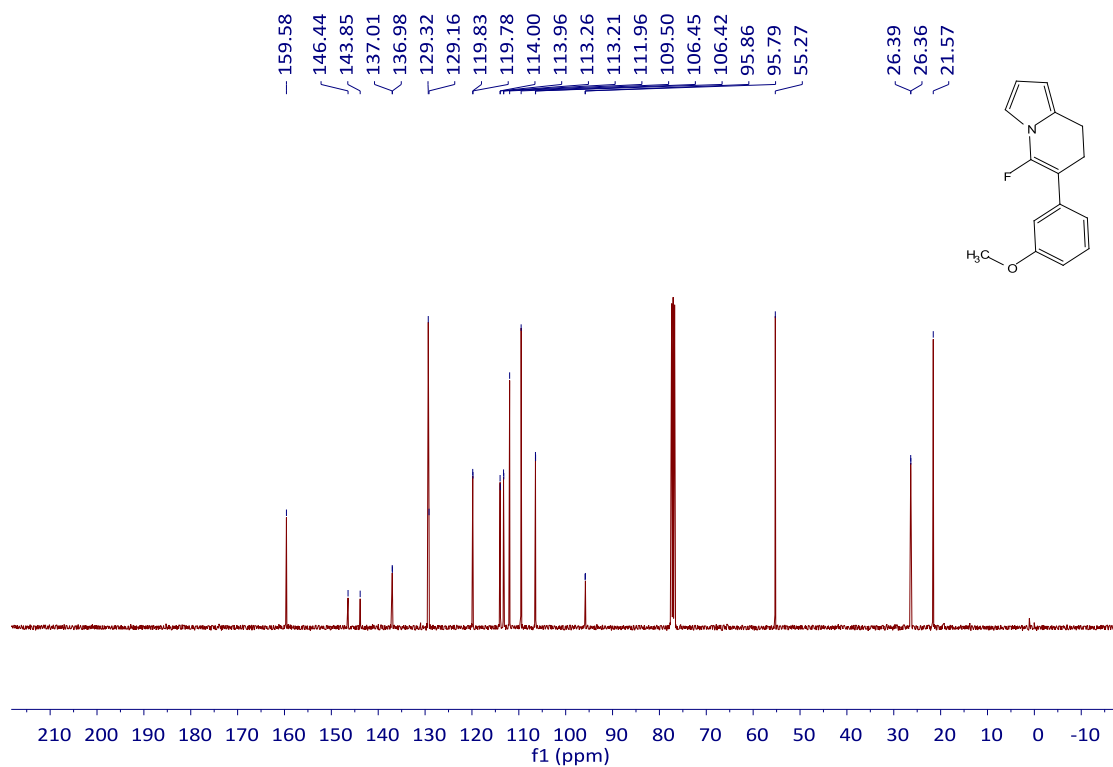
$^{13}\text{C}\{^1\text{H}\}$ NMR of **4j** (100 Hz, CDCl_3)



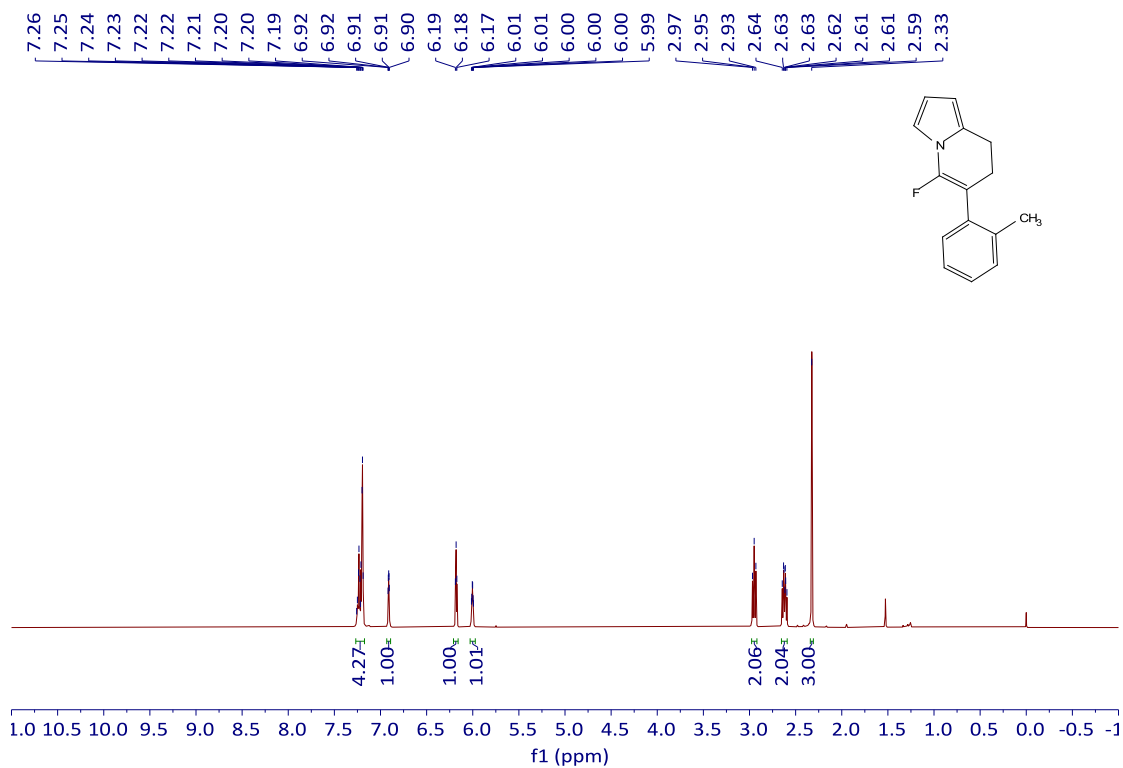
¹H NMR of **4k** (400 Hz, CDCl₃)



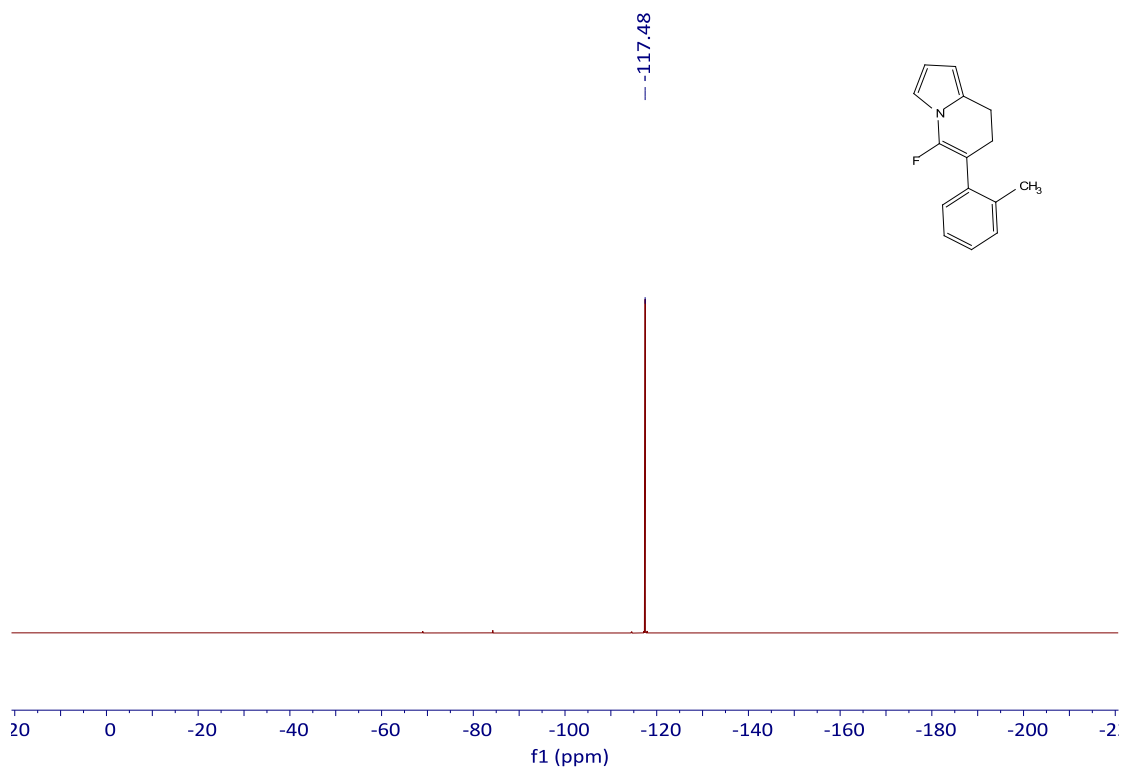
¹⁹F NMR of **4k** (376 Hz, CDCl₃)



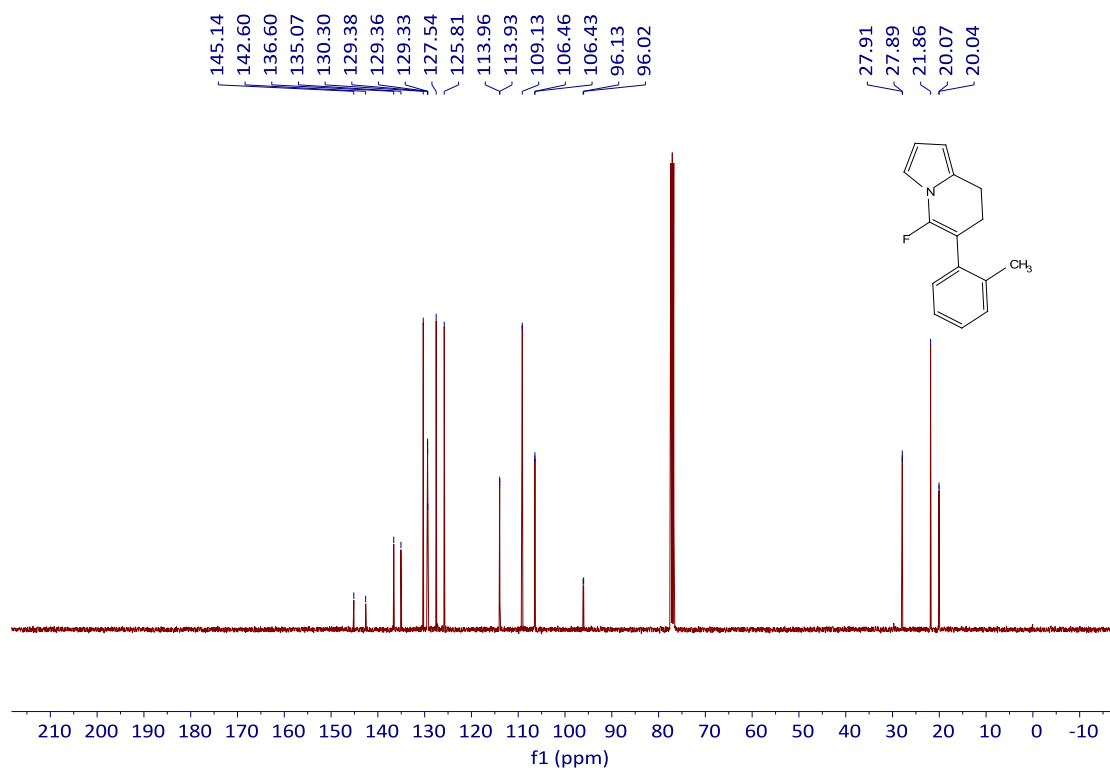
$^{13}\text{C}\{^1\text{H}\}$ NMR of **4k** (100 Hz, CDCl_3)



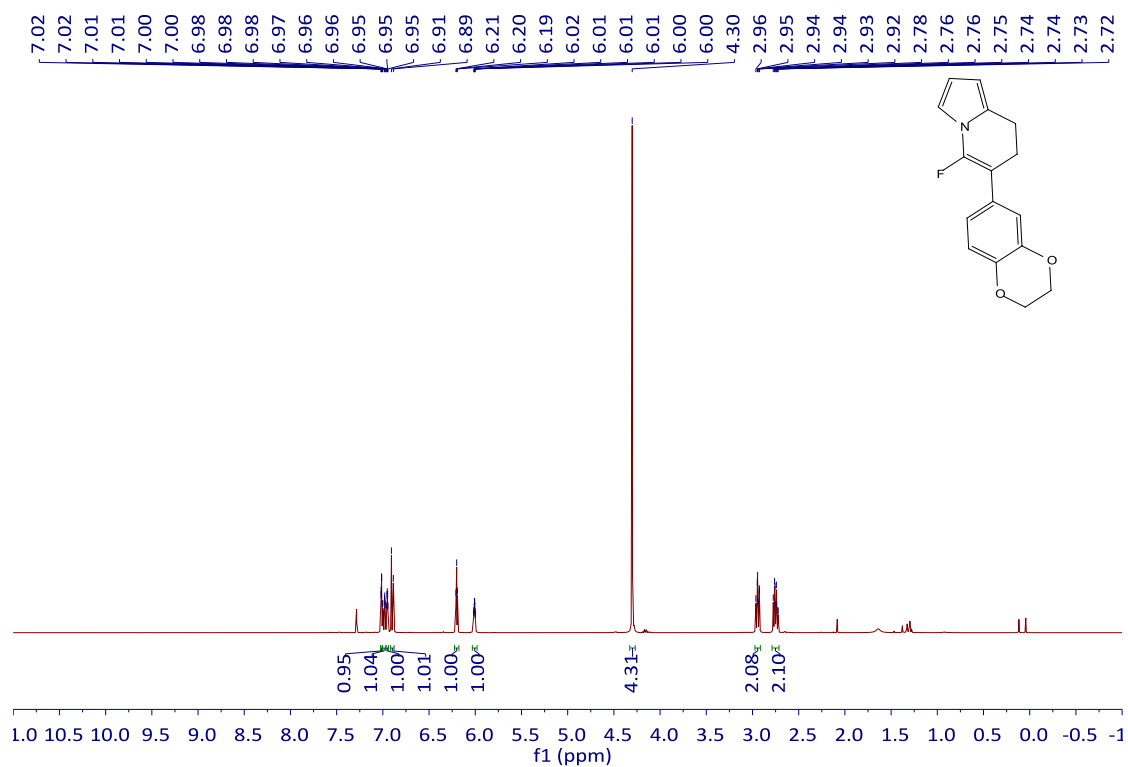
^1H NMR of **4l** (400 Hz, CDCl_3)



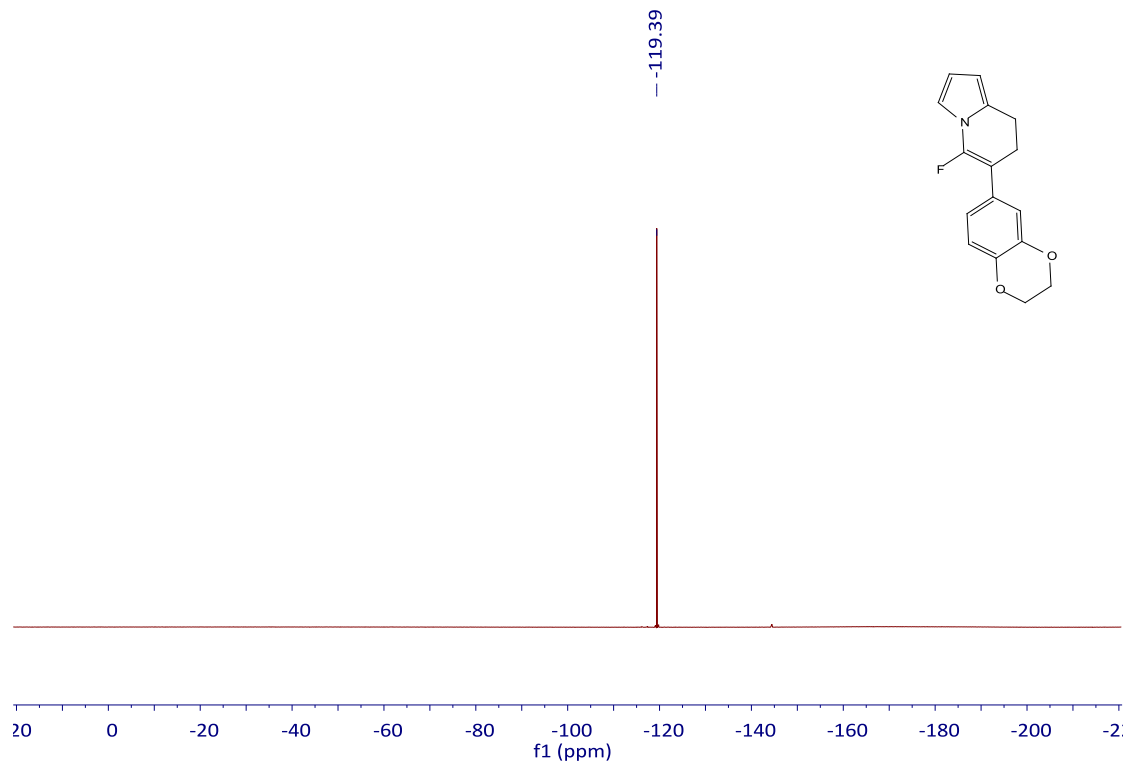
^{19}F NMR of **4I** (376 Hz, CDCl_3)



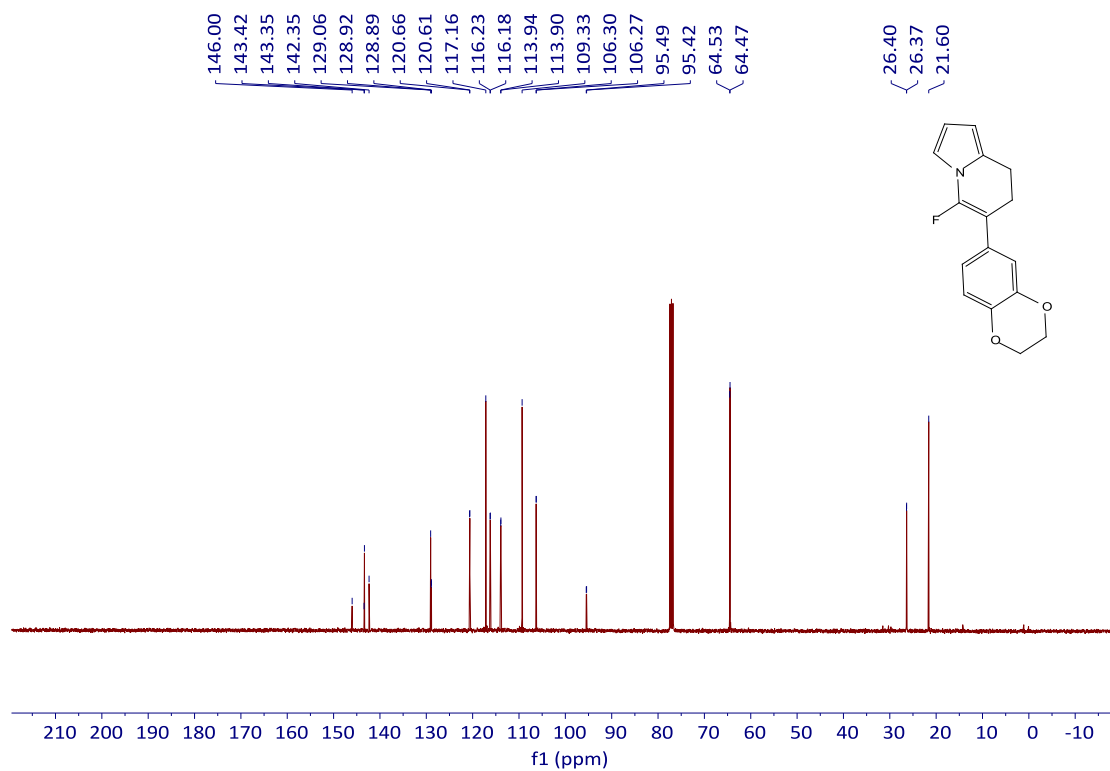
$^{13}\text{C}\{^1\text{H}\}$ NMR of **4I** (100 Hz, CDCl_3)



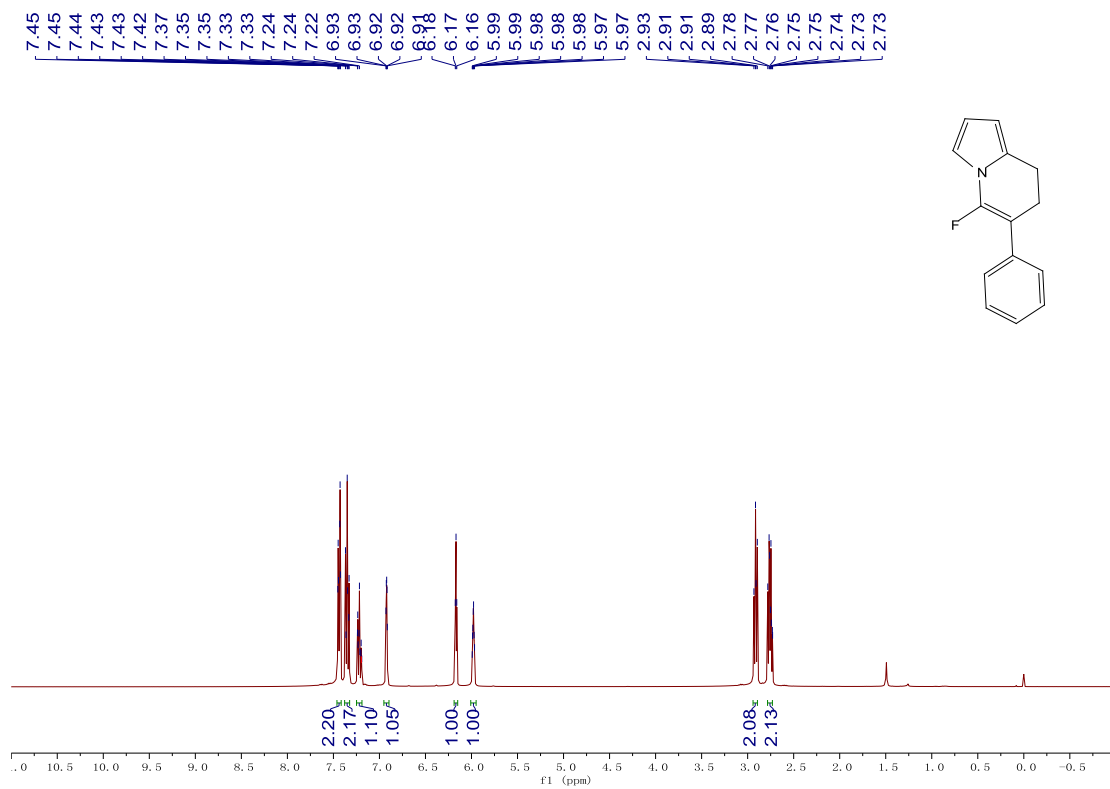
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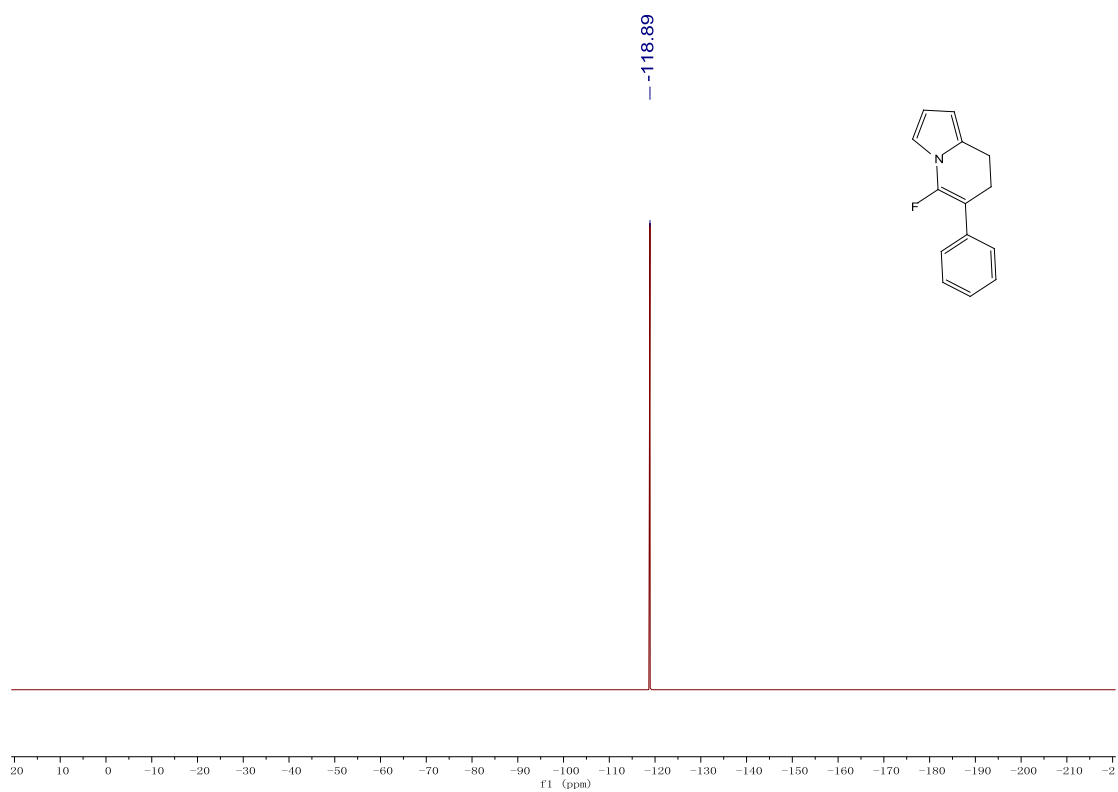
¹⁹F NMR of **4m** (376 Hz, CDCl₃)



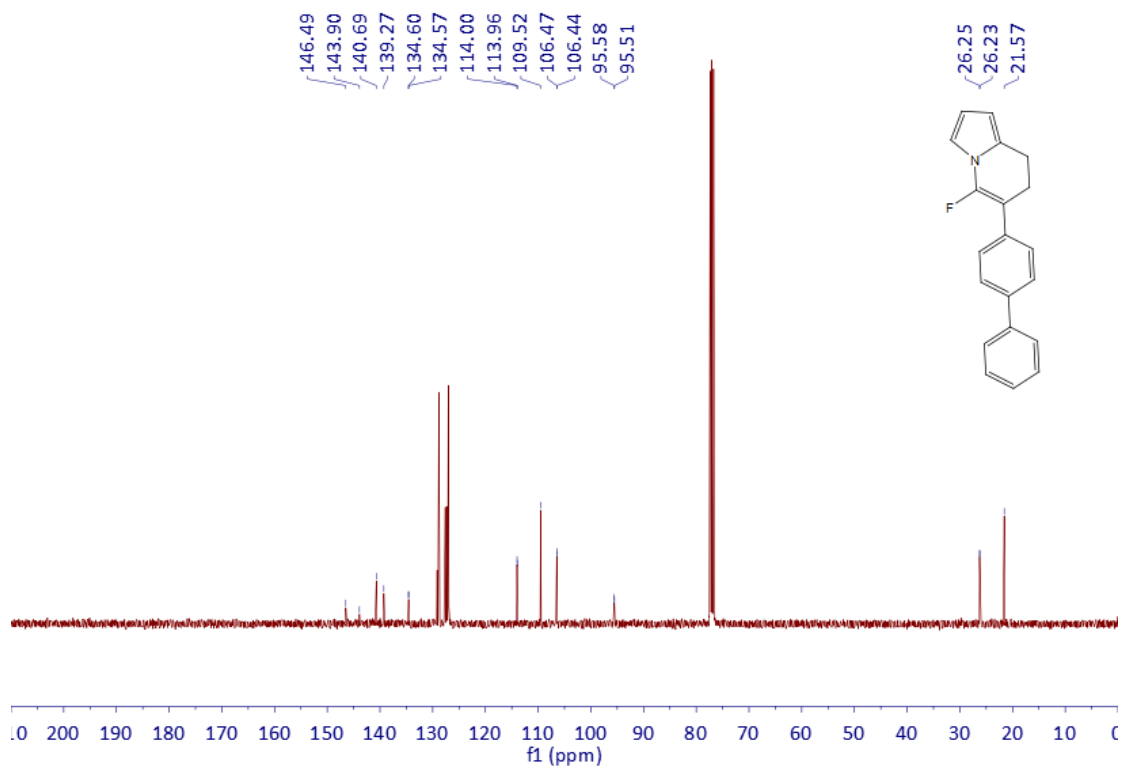
¹³C{¹H} NMR of **4m** (100 Hz, CDCl₃)



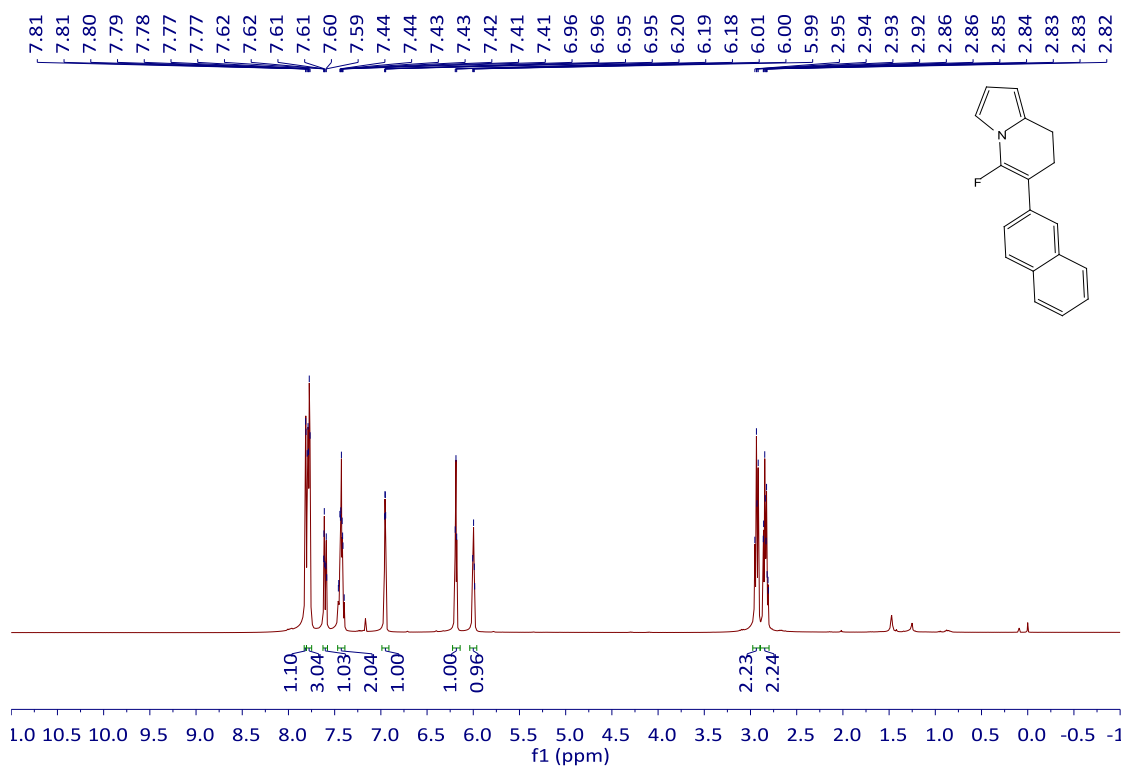
¹H NMR of **4n** (400 Hz, CDCl₃)



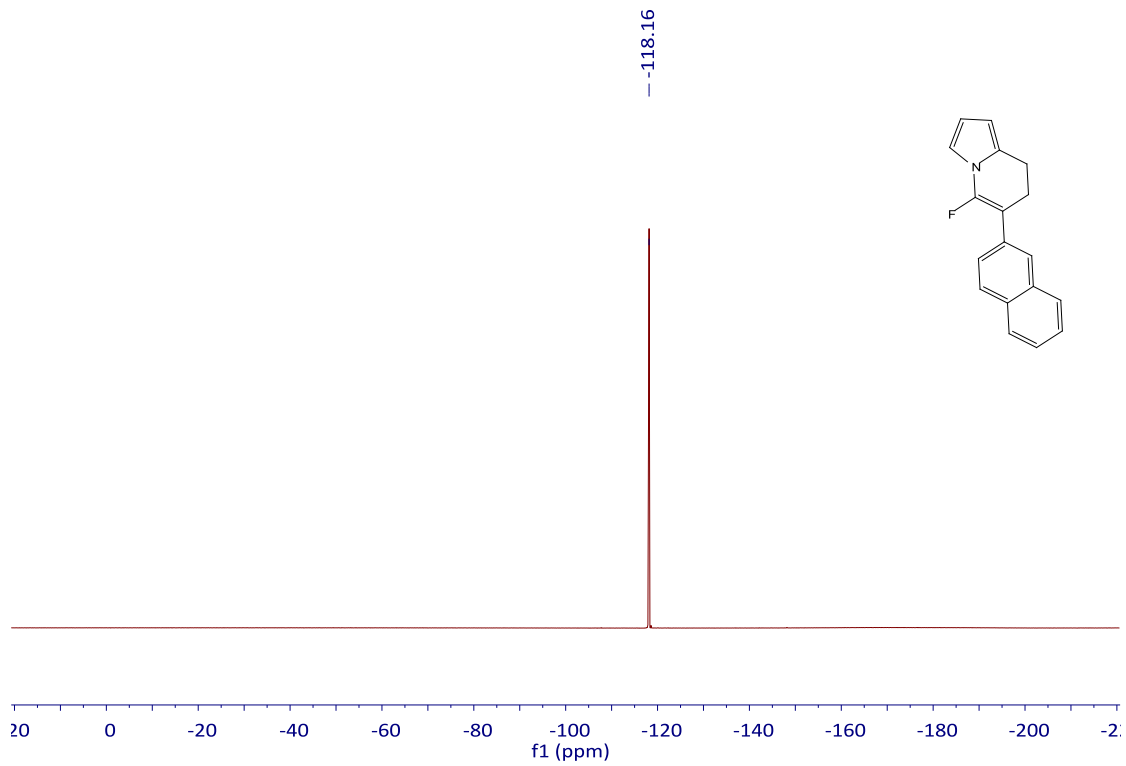
^{19}F NMR of **4n** (376 Hz, CDCl_3)



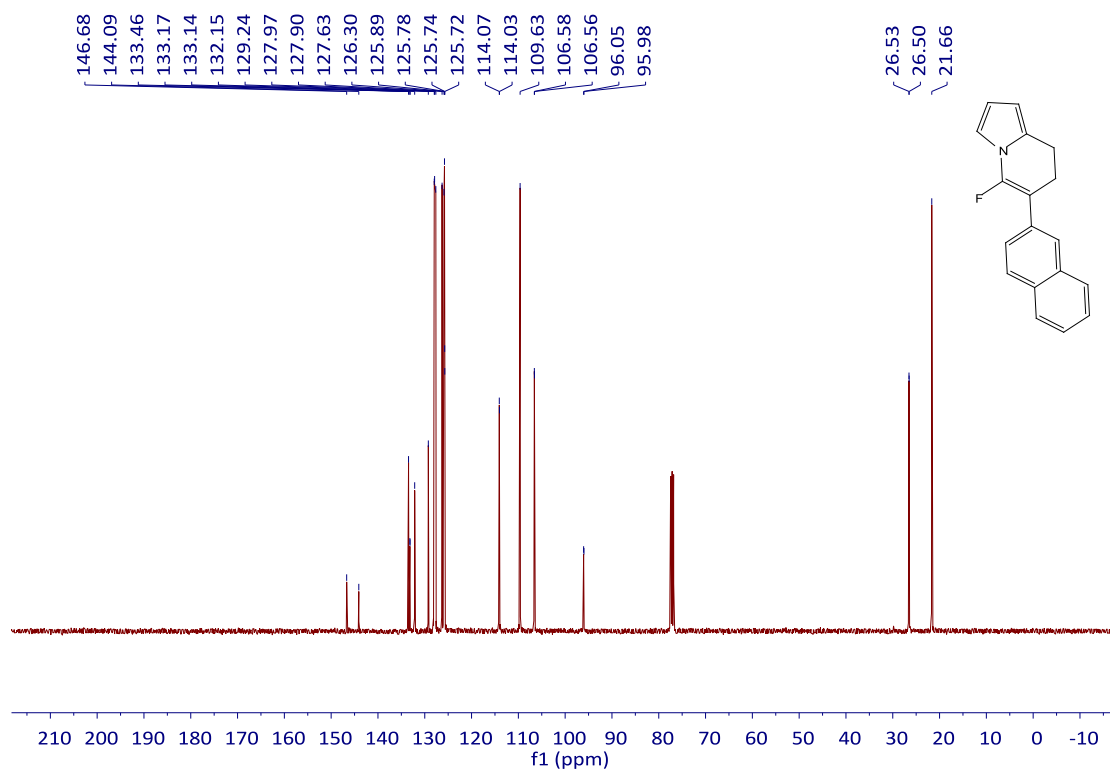
$^{13}\text{C}\{^1\text{H}\}$ NMR of **4n** (100 Hz, CDCl_3)



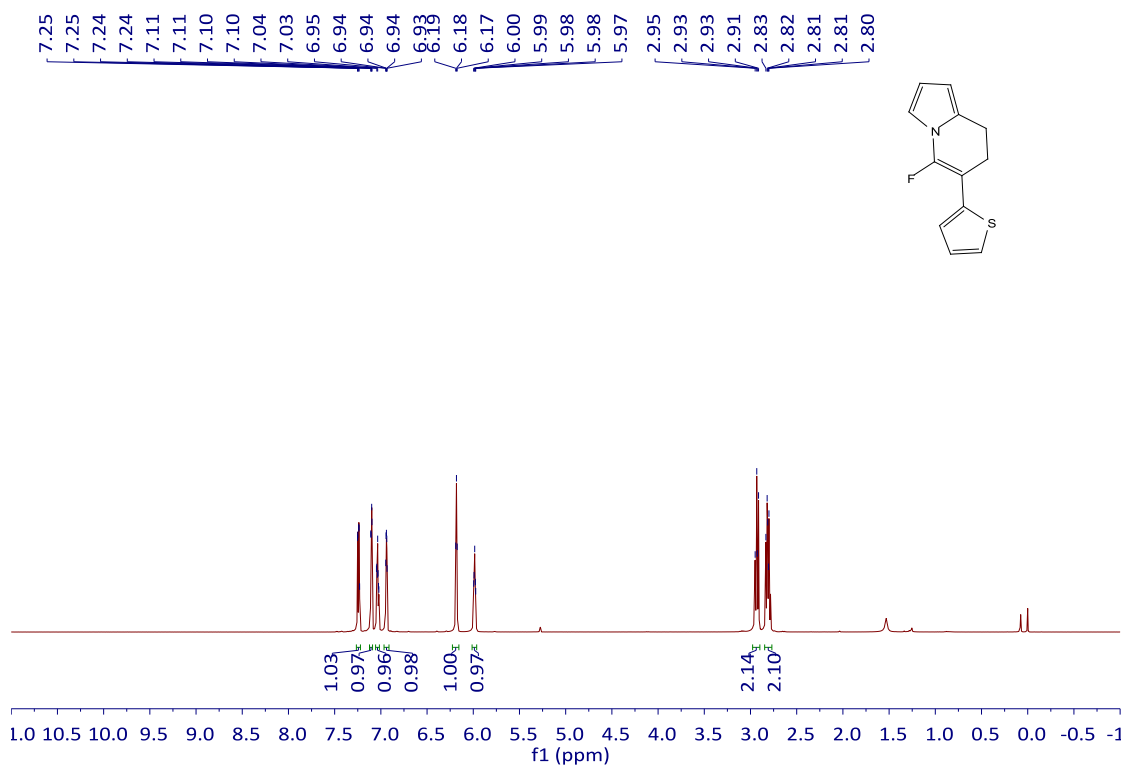
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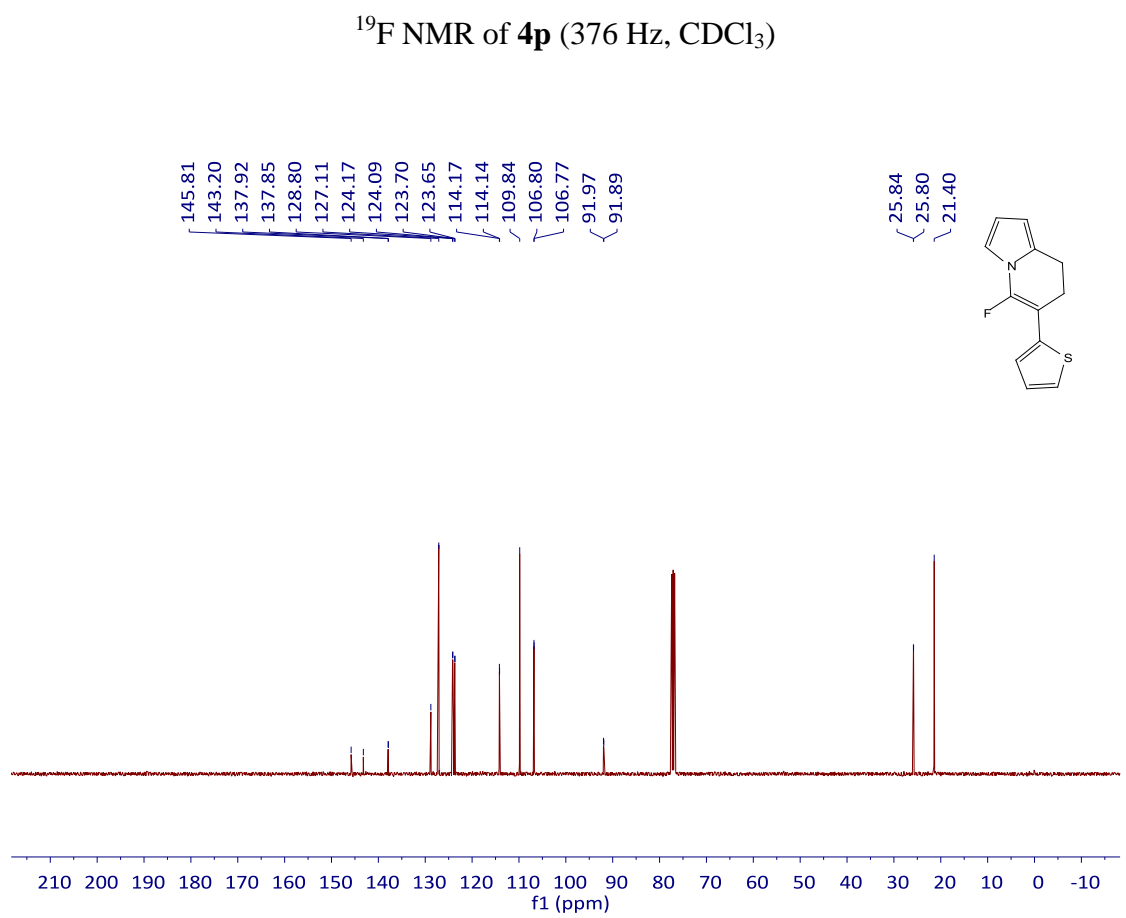
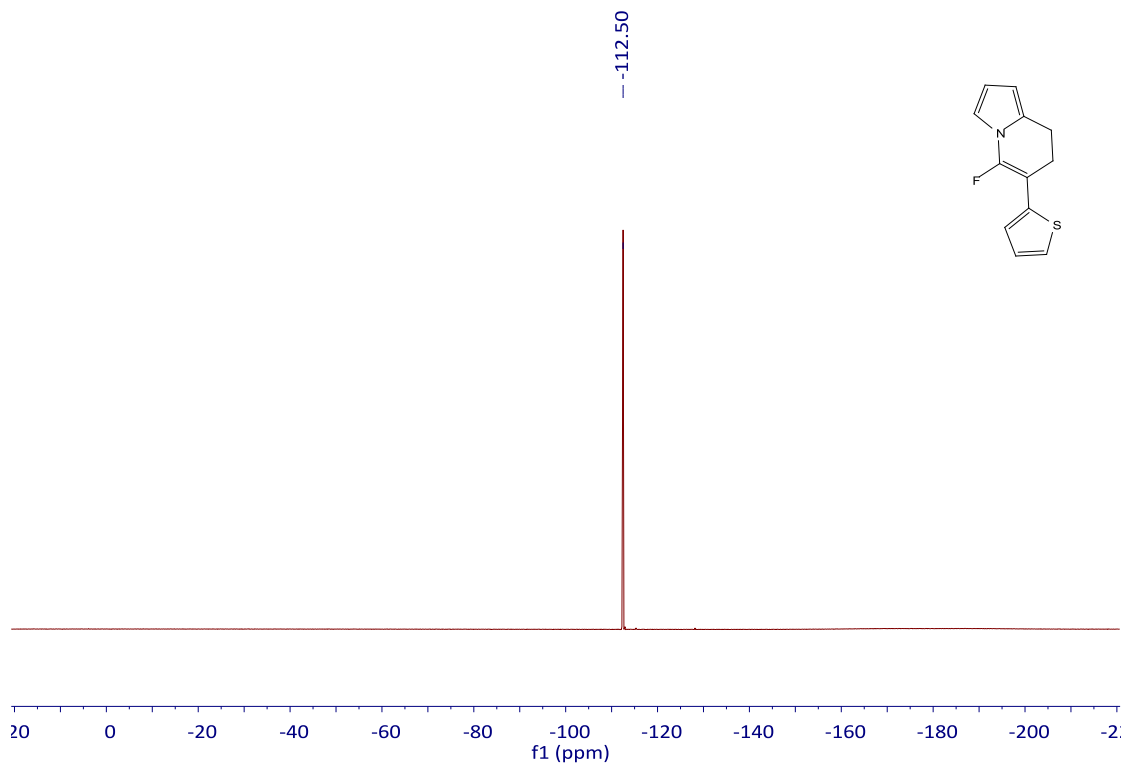
¹⁹F NMR of **4o** (376 Hz, CDCl₃)

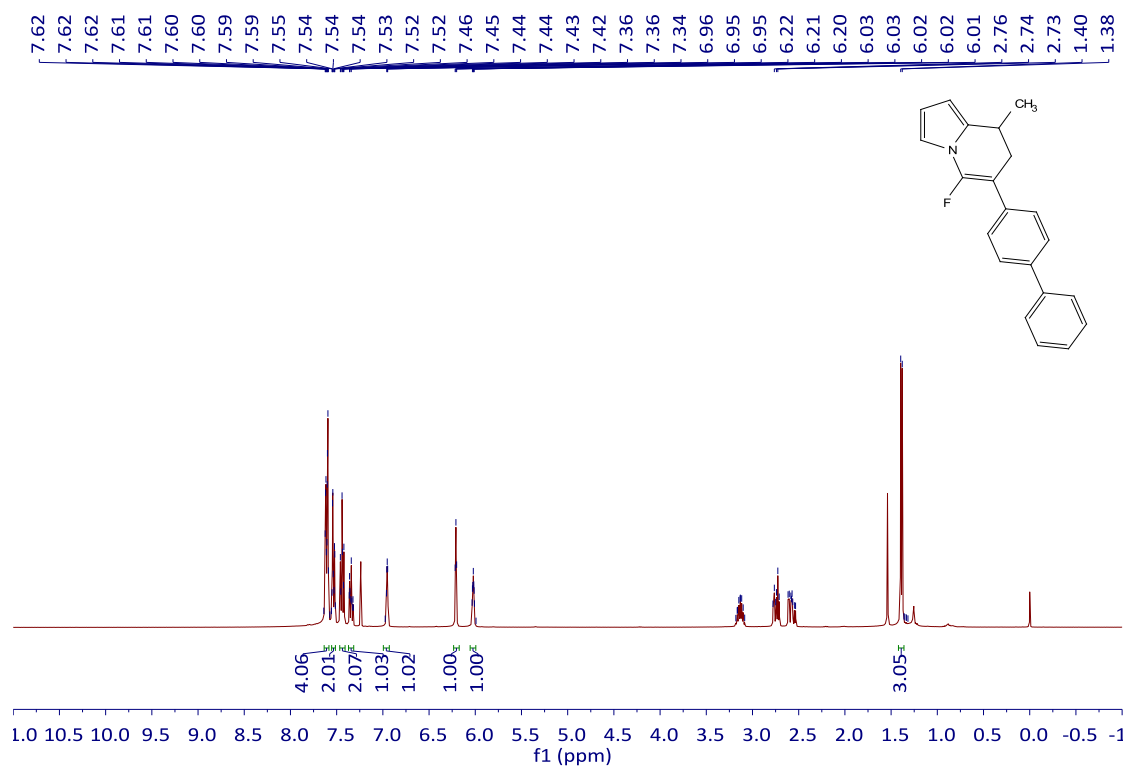


$^{13}\text{C}\{^1\text{H}\}$ NMR of **4o** (100 Hz, CDCl_3)

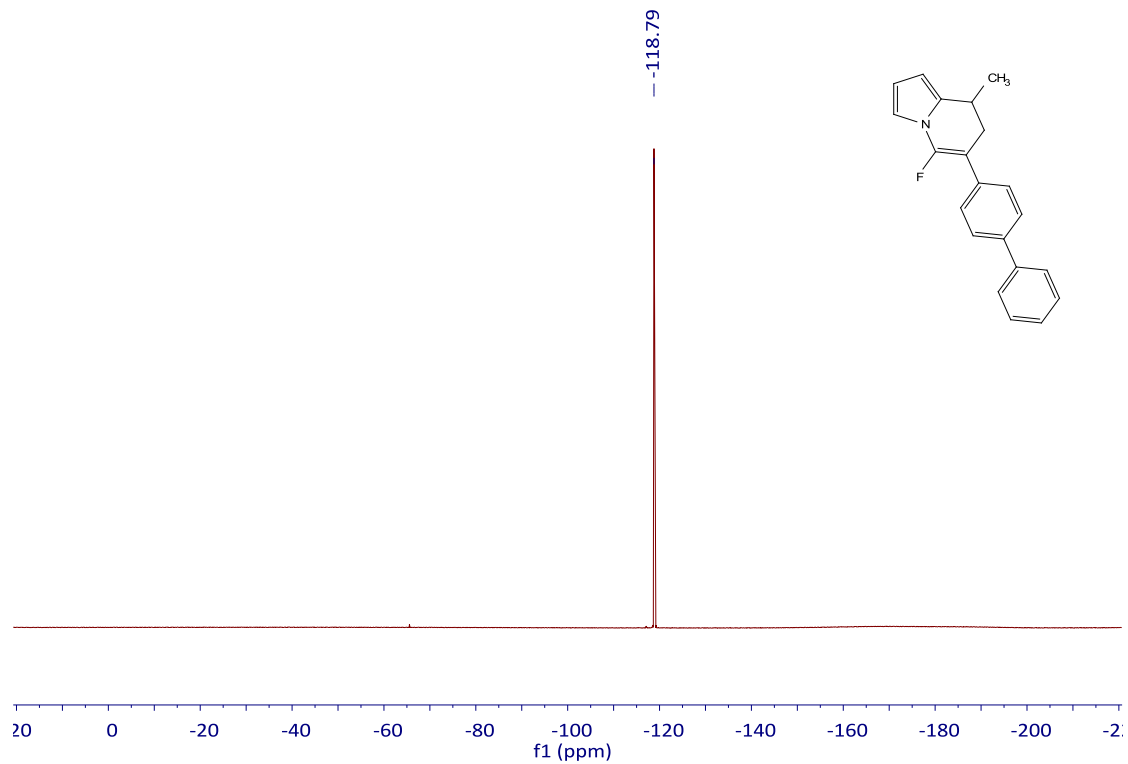


^1H NMR of **4p** (400 Hz, CDCl_3)

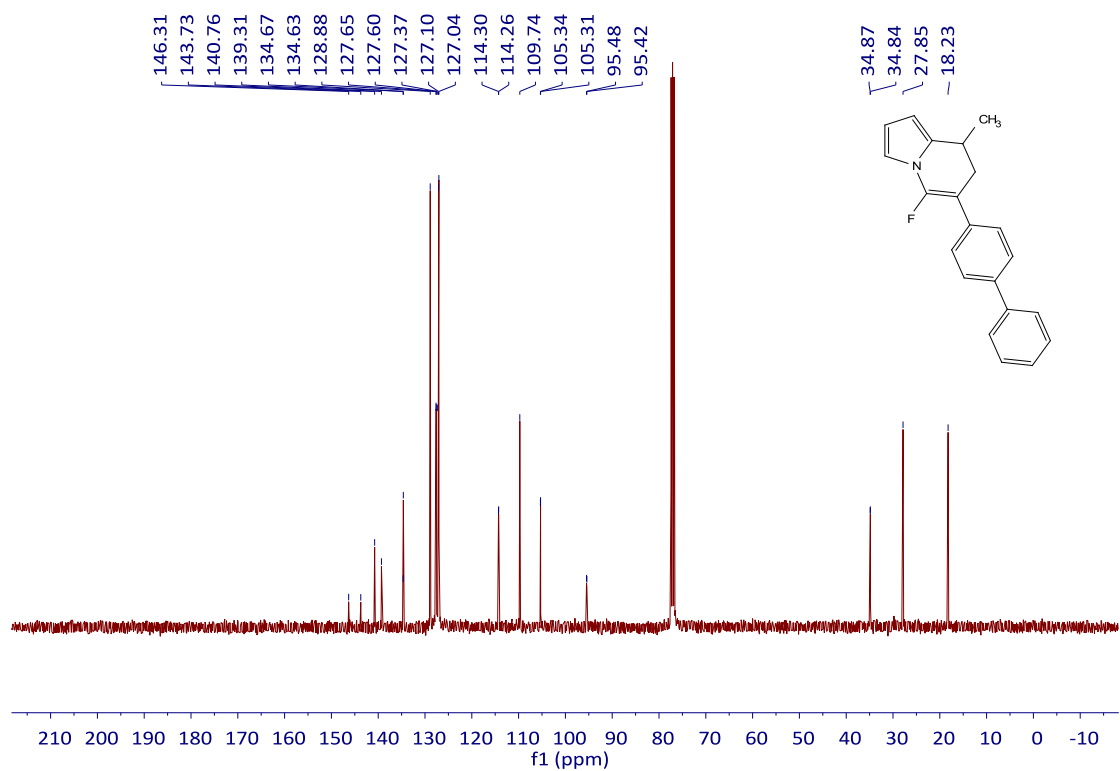




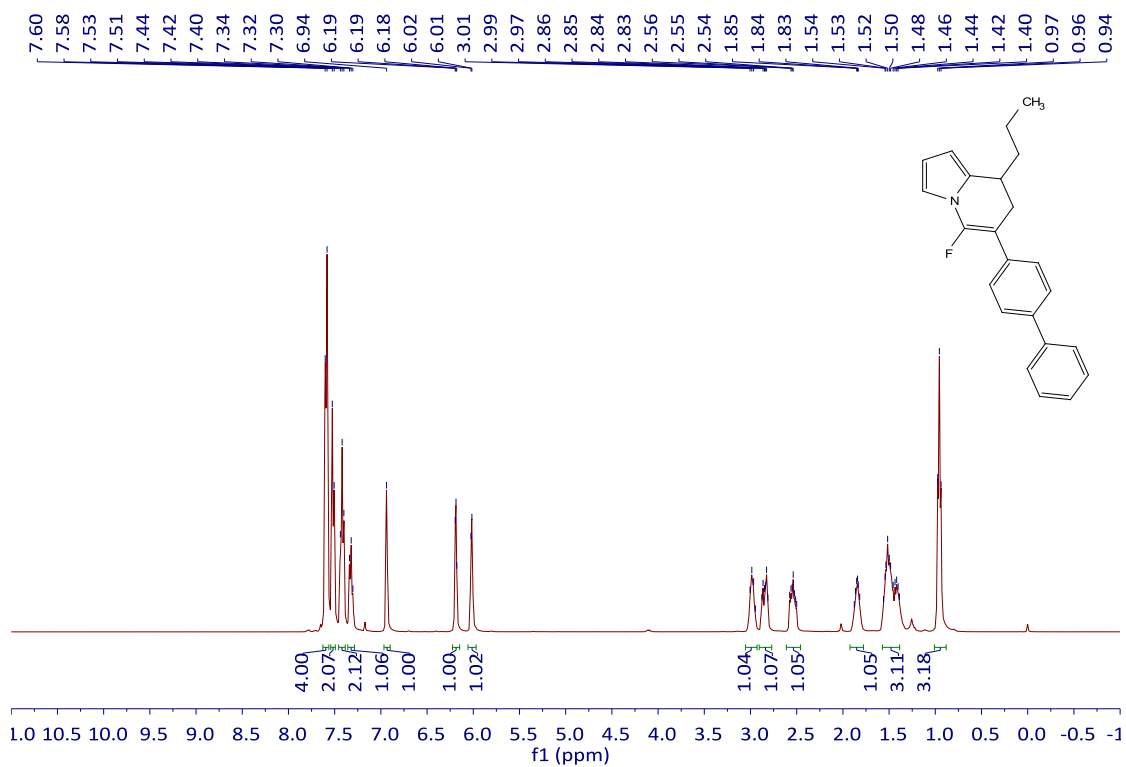
¹H NMR of **4q** (400 Hz, CDCl₃)



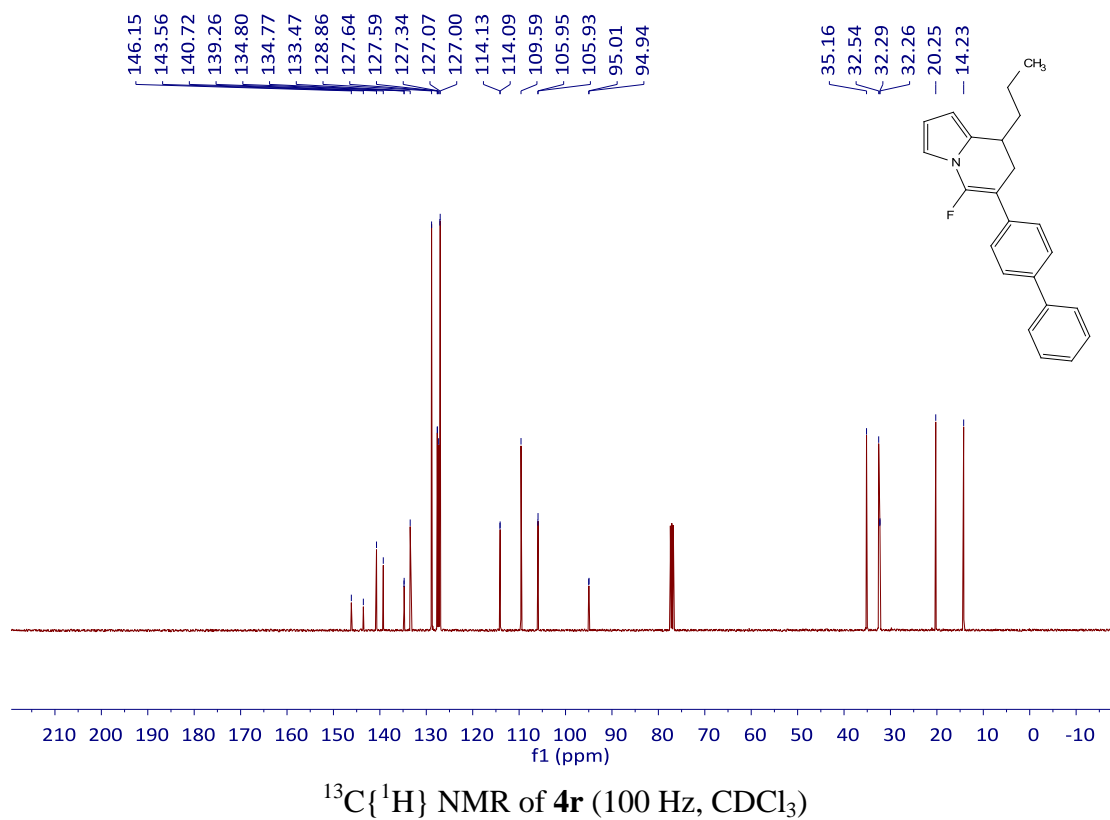
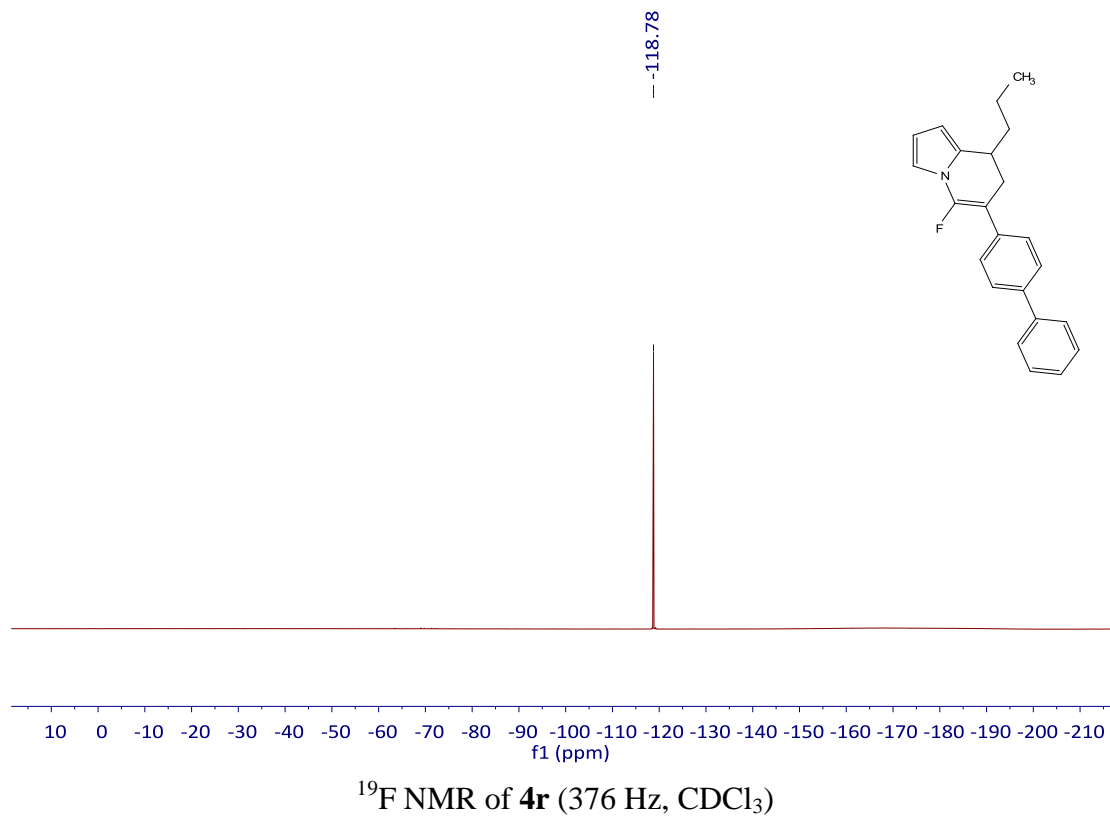
¹⁹F NMR of **4q** (376 Hz, CDCl₃)

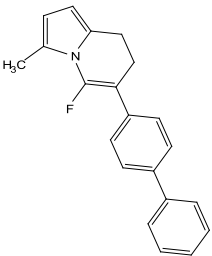
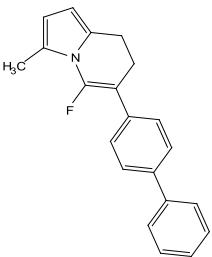


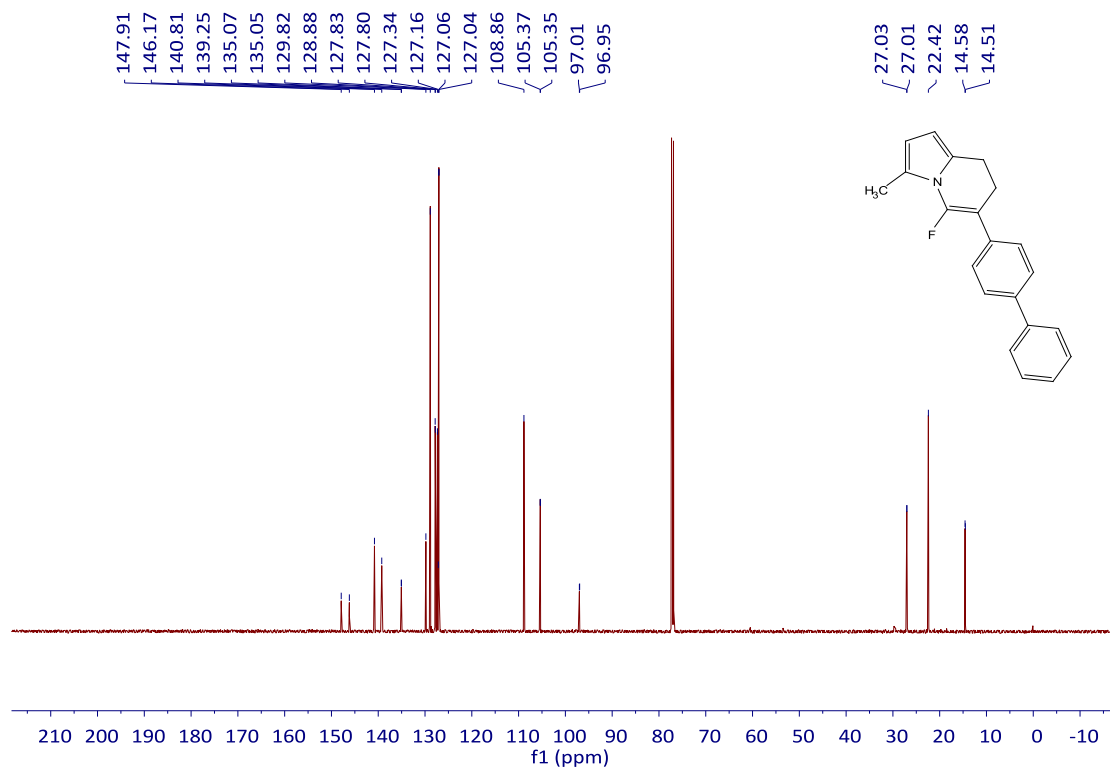
¹³C{¹H} NMR of **4q** (100 Hz, CDCl₃)



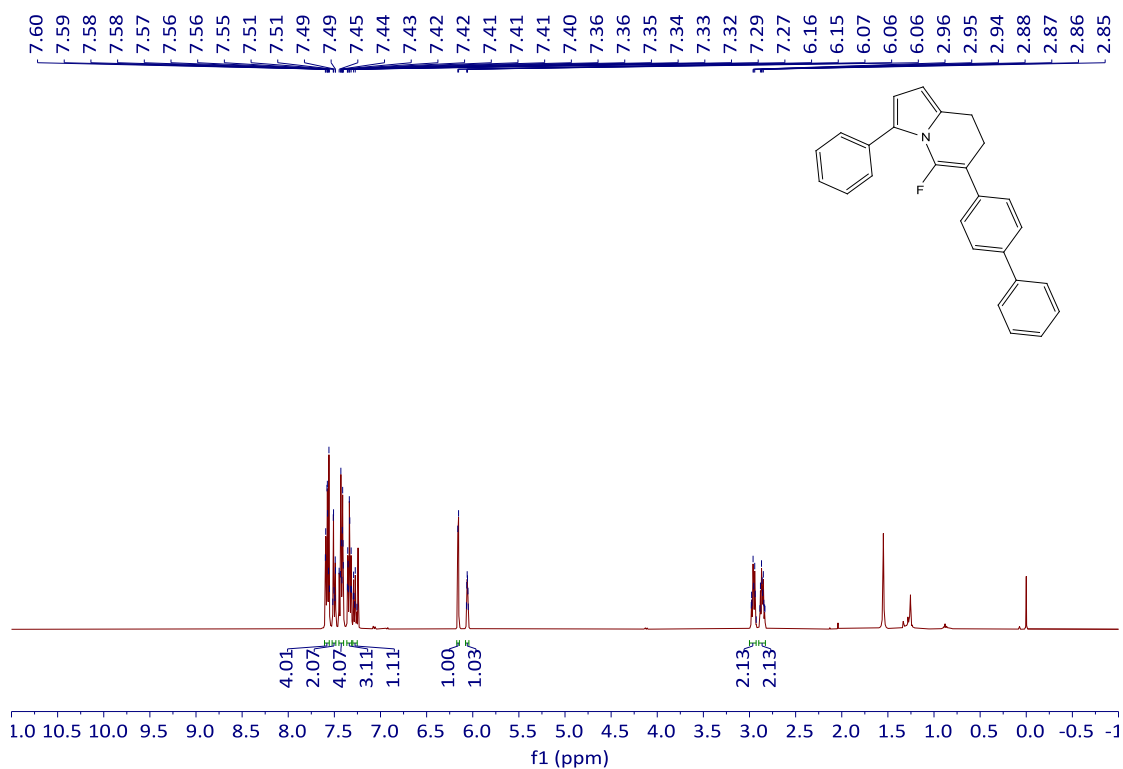
¹H NMR of **4r** (400 Hz, CDCl₃)



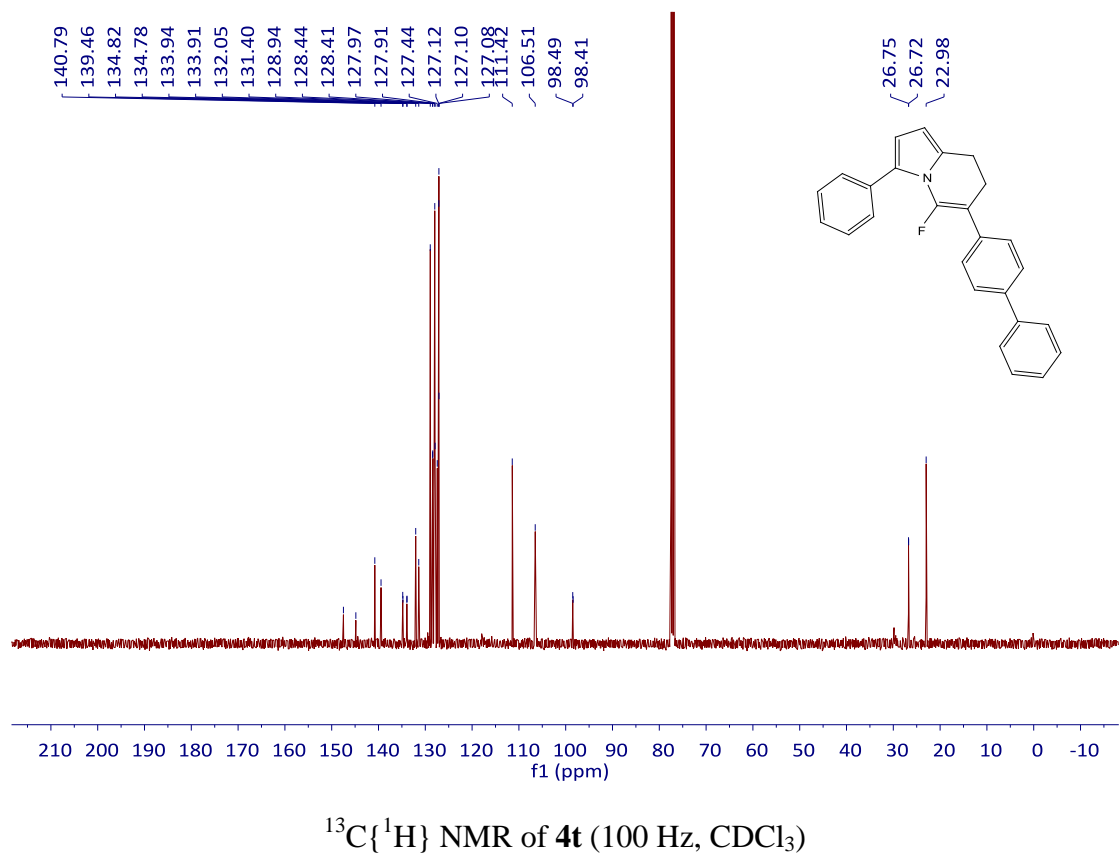
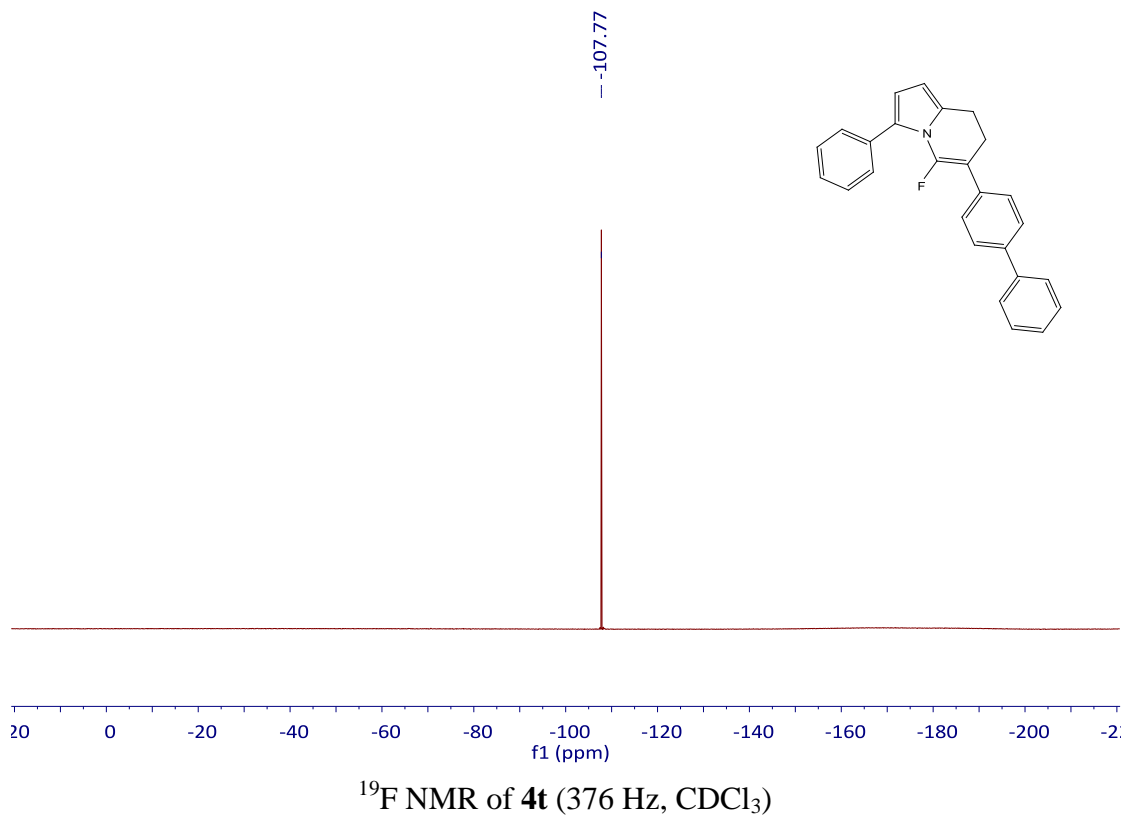


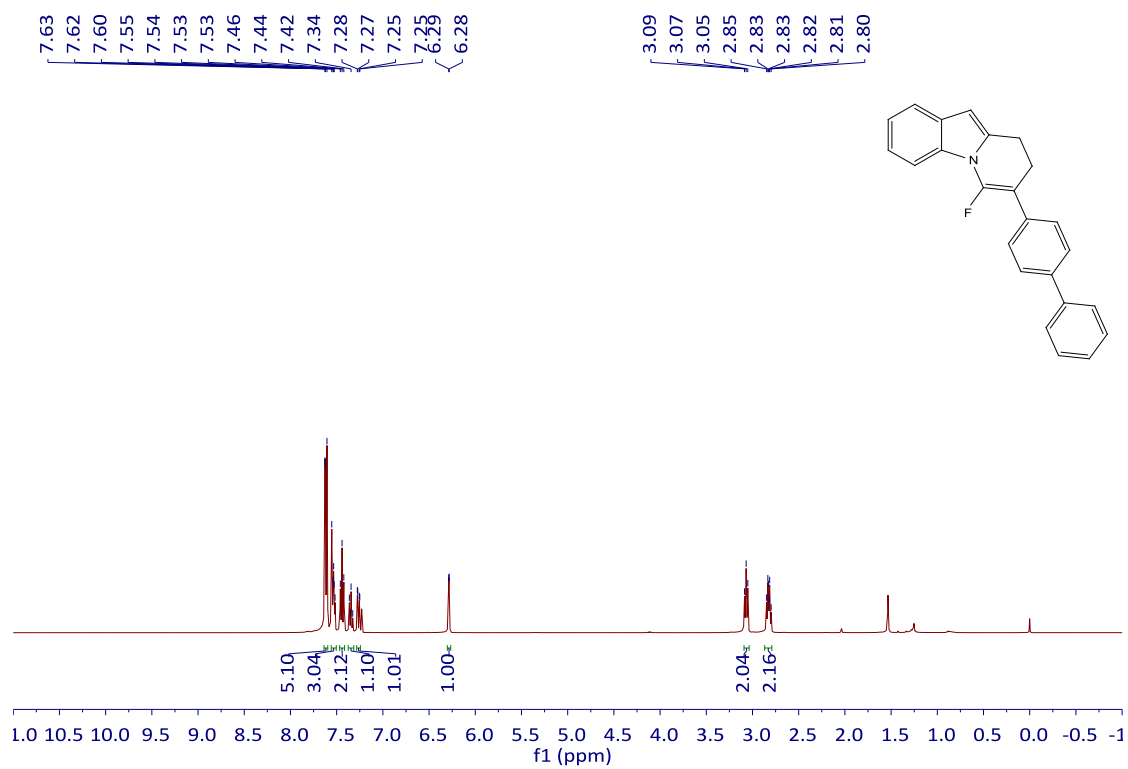


¹³C{¹H} NMR of **4s** (100 Hz, CDCl₃)

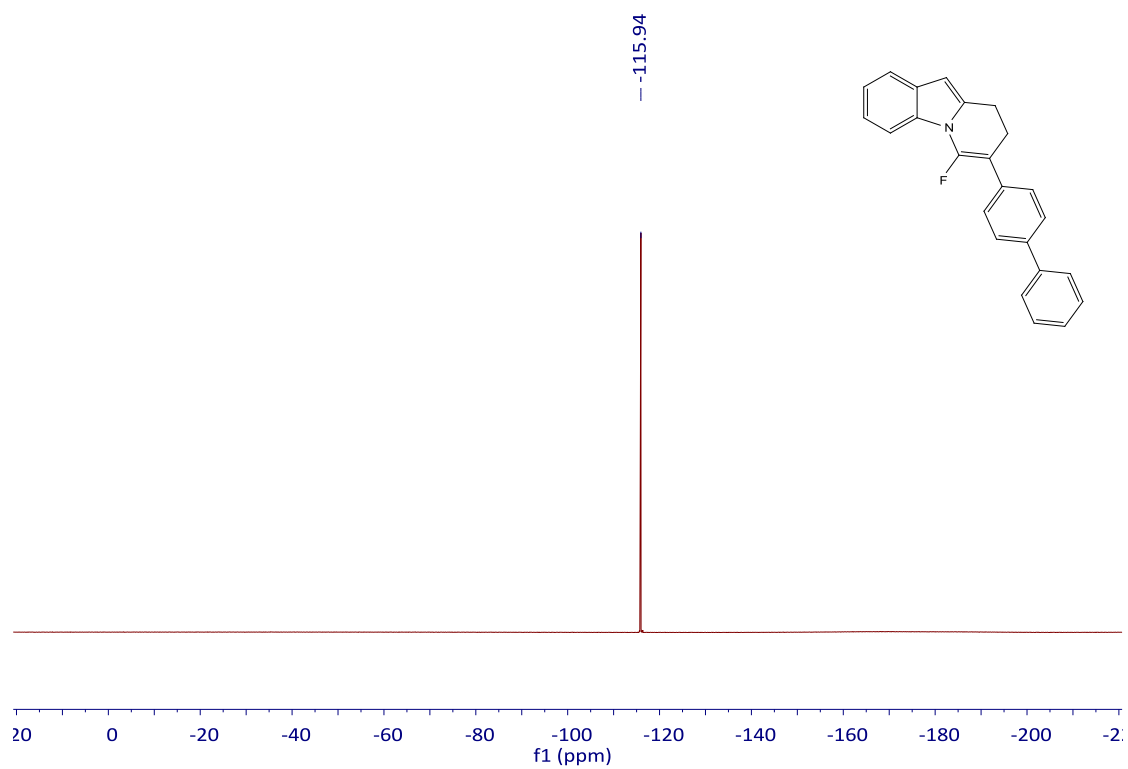


¹H NMR of **4t** (400 Hz, CDCl₃)

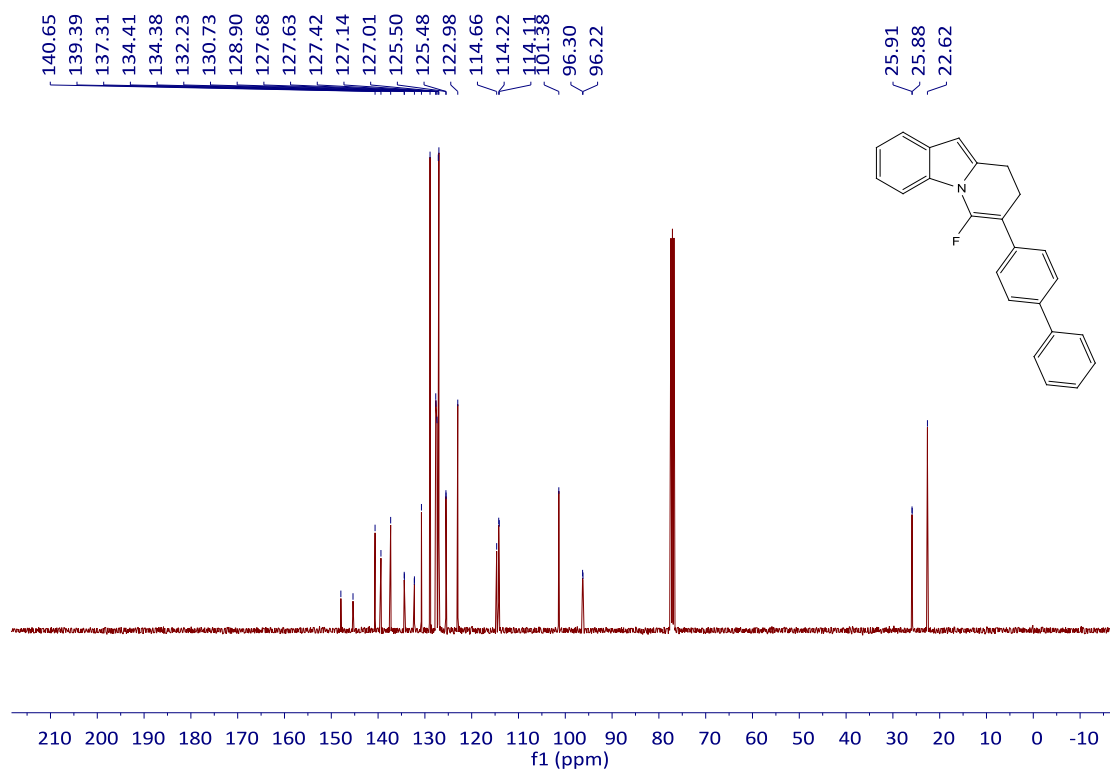




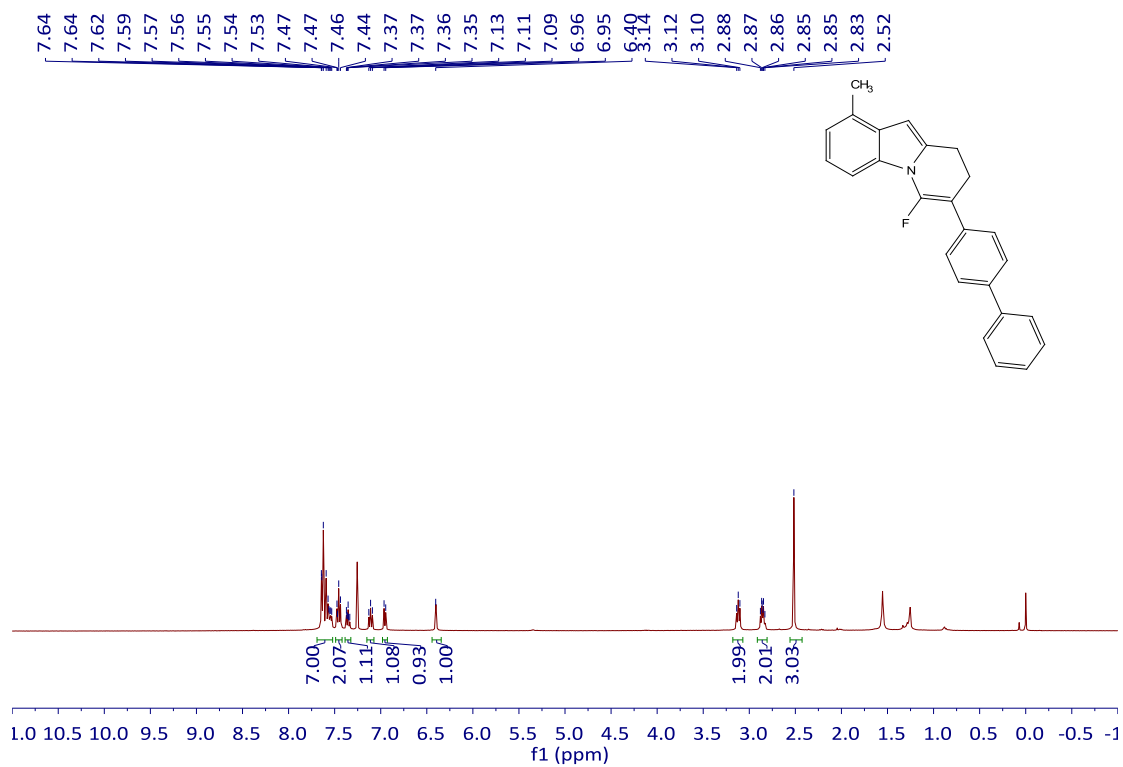
¹H NMR of **4u** (400 Hz, CDCl₃)



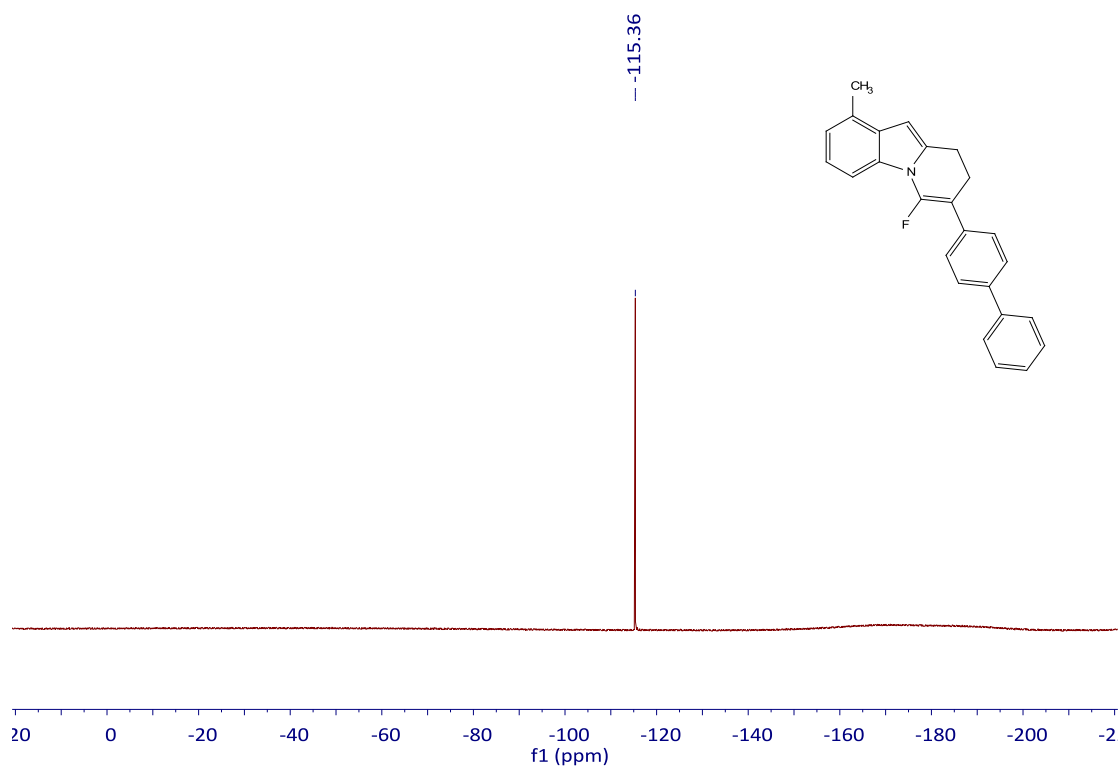
¹⁹F NMR of **4u** (376 Hz, CDCl₃)



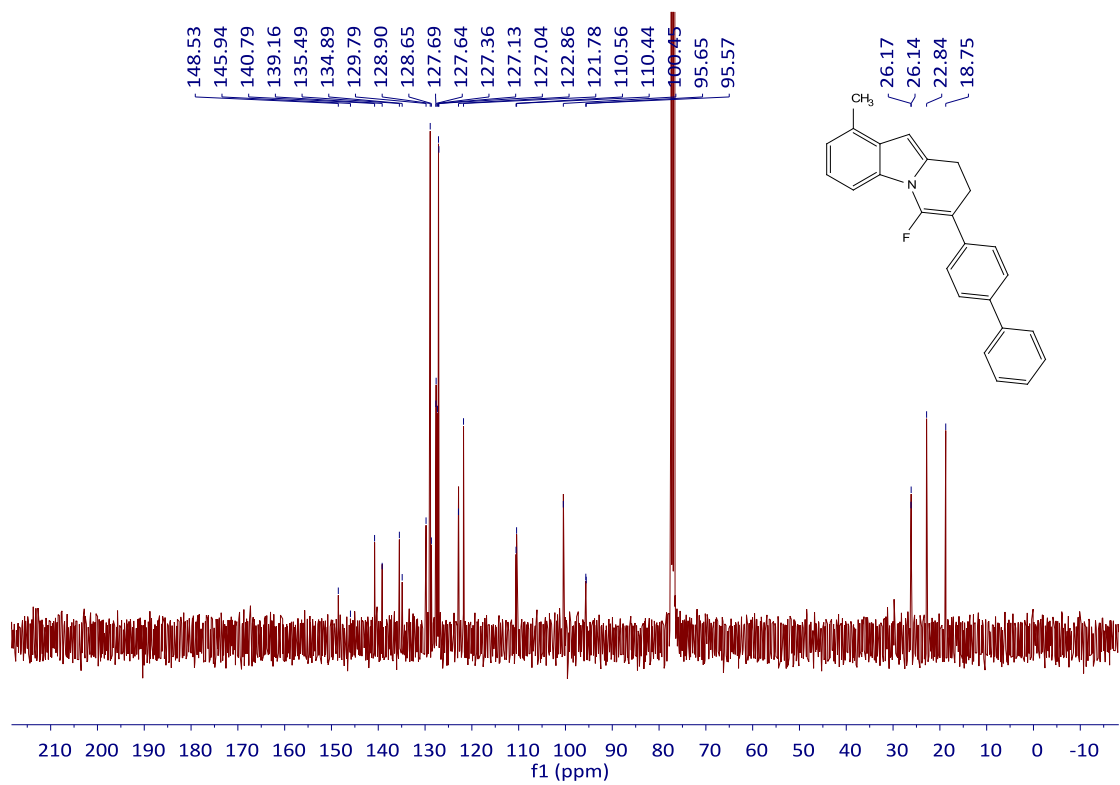
¹³C{¹H} NMR of **4u** (100 Hz, CDCl₃)



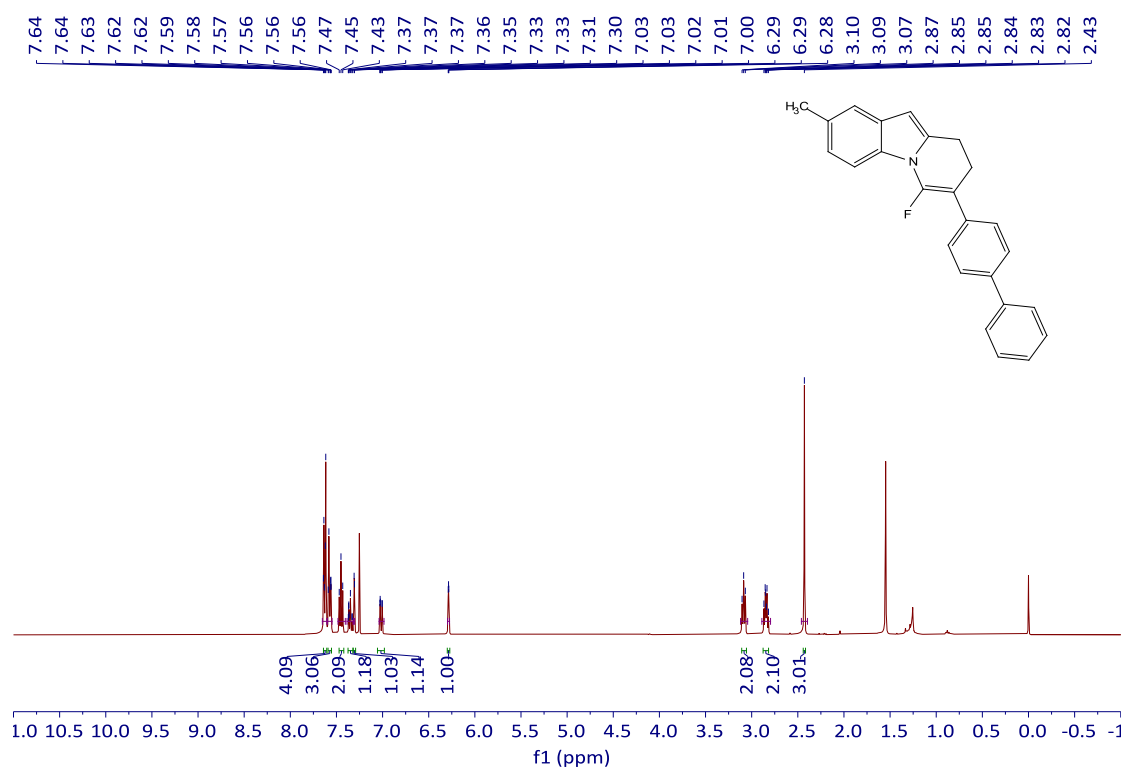
¹H NMR of **4v** (400 Hz, CDCl₃)



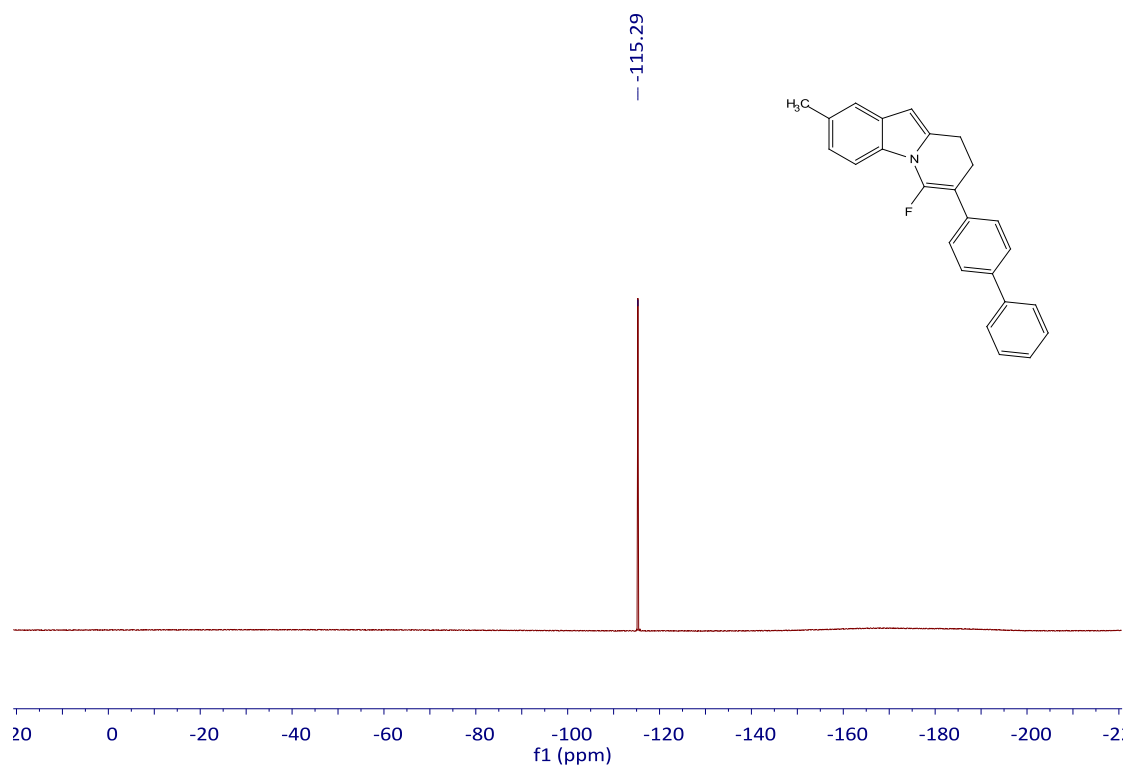
^{19}F NMR of **4v** (376 Hz, CDCl_3)



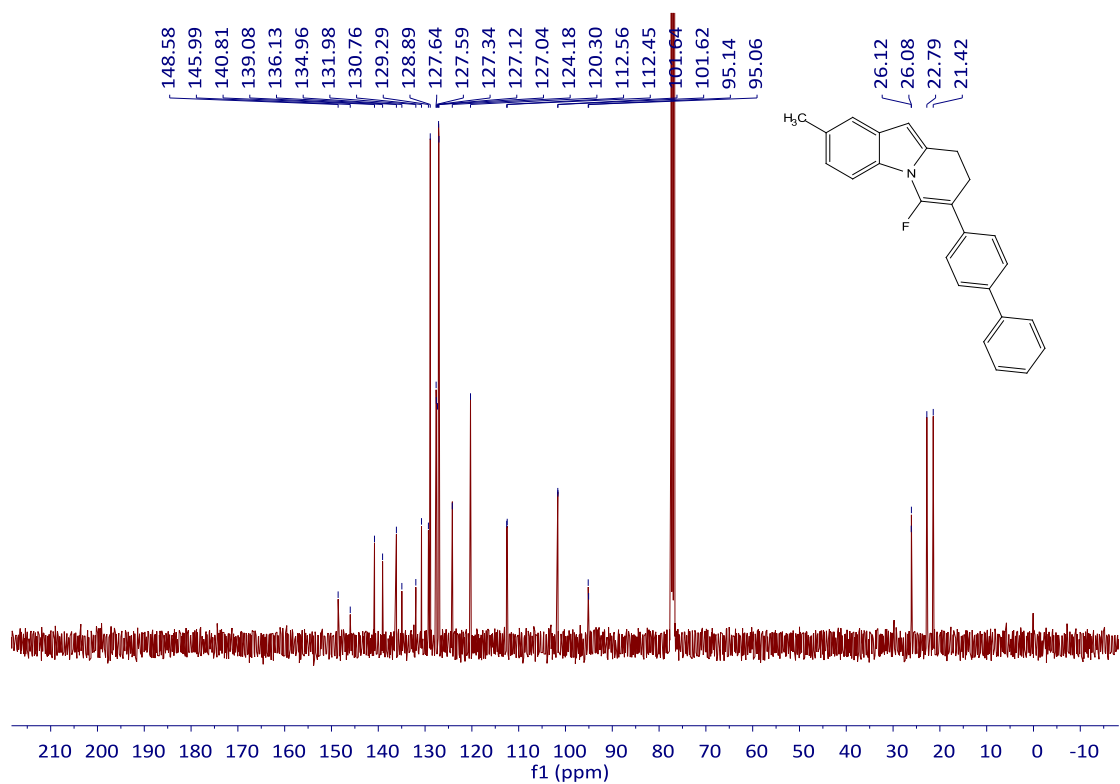
$^{13}\text{C}\{^1\text{H}\}$ NMR of **4v** (100 Hz, CDCl_3)



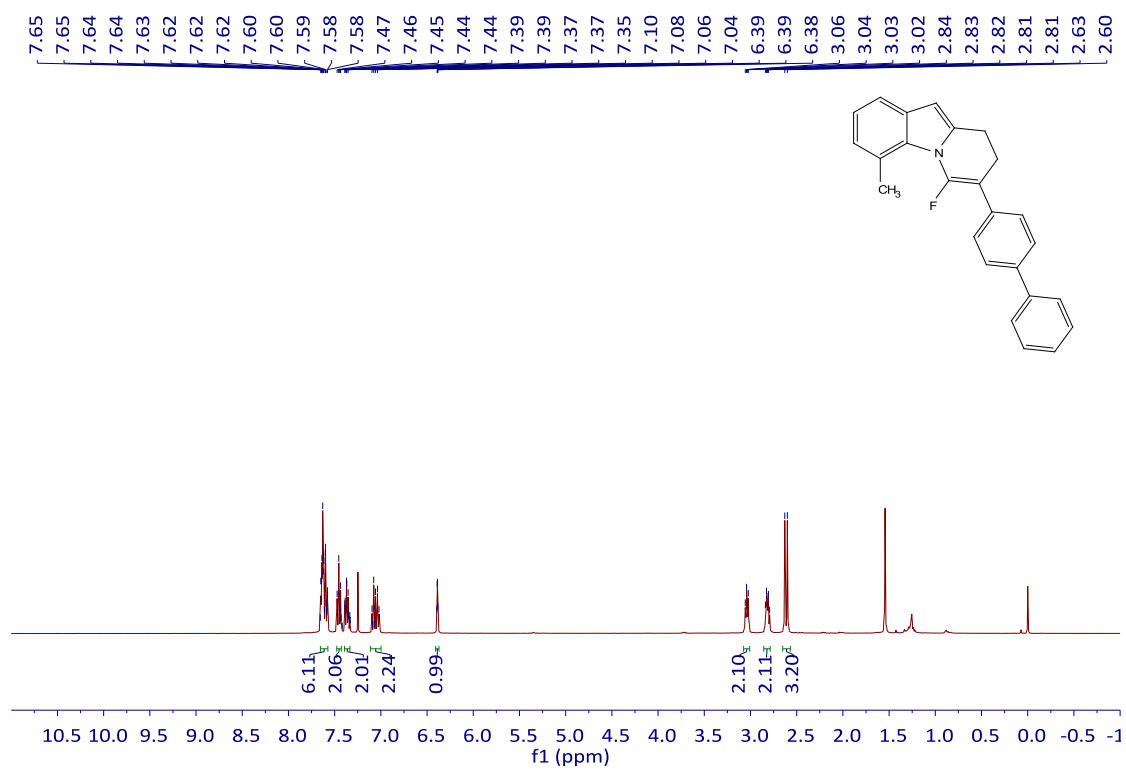
¹H NMR of **4w** (400 Hz, CDCl₃)



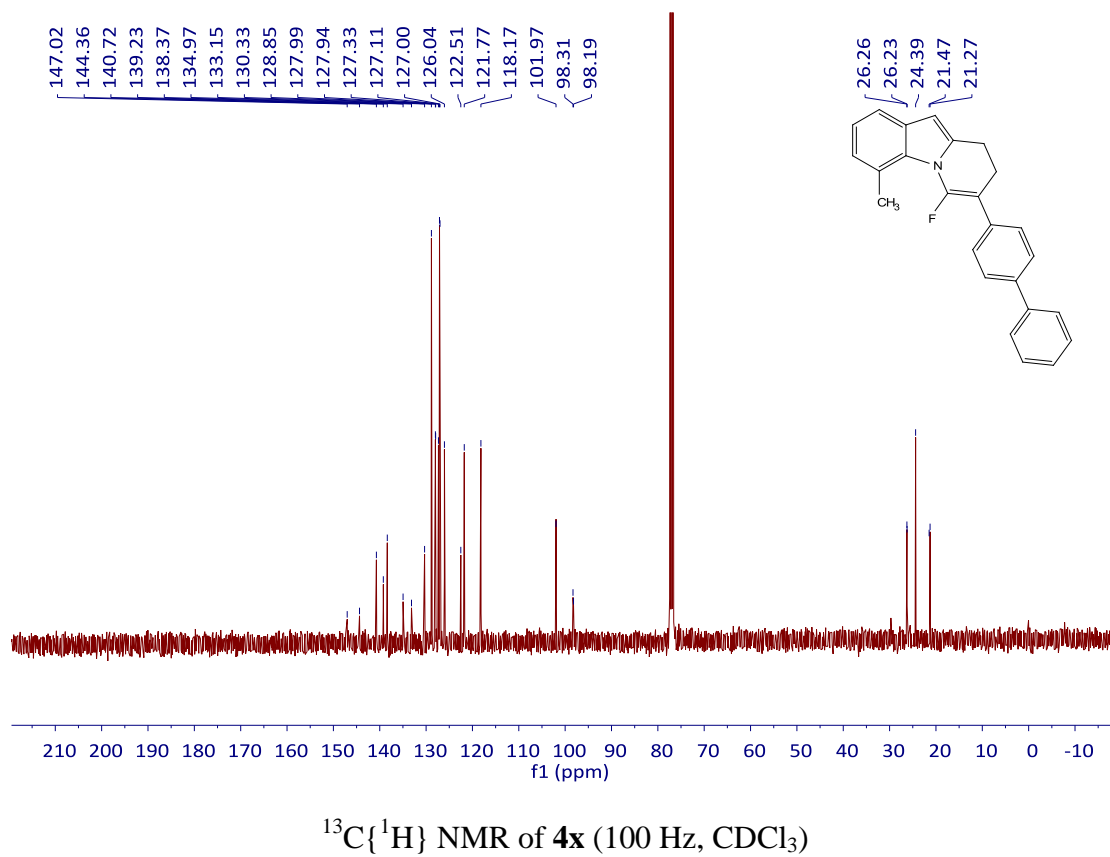
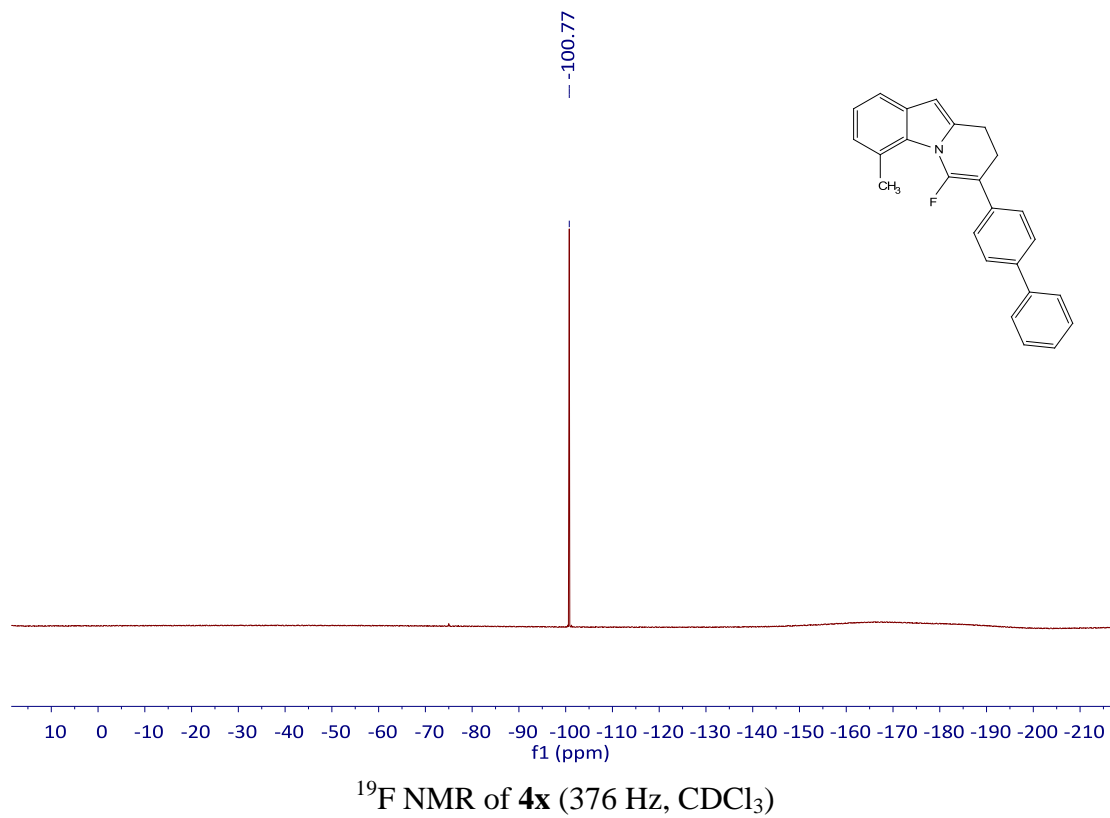
¹⁹F NMR of **4w** (376 Hz, CDCl₃)

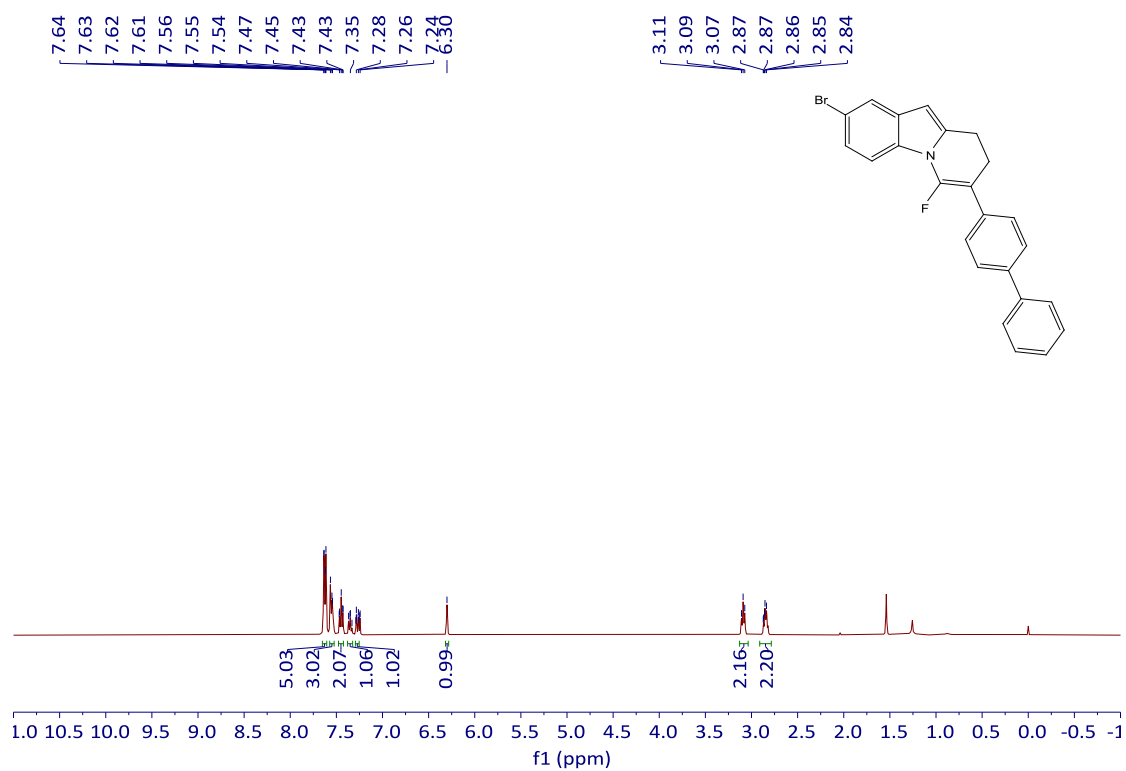


¹³C{¹H} NMR of **4w** (100 Hz, CDCl₃)

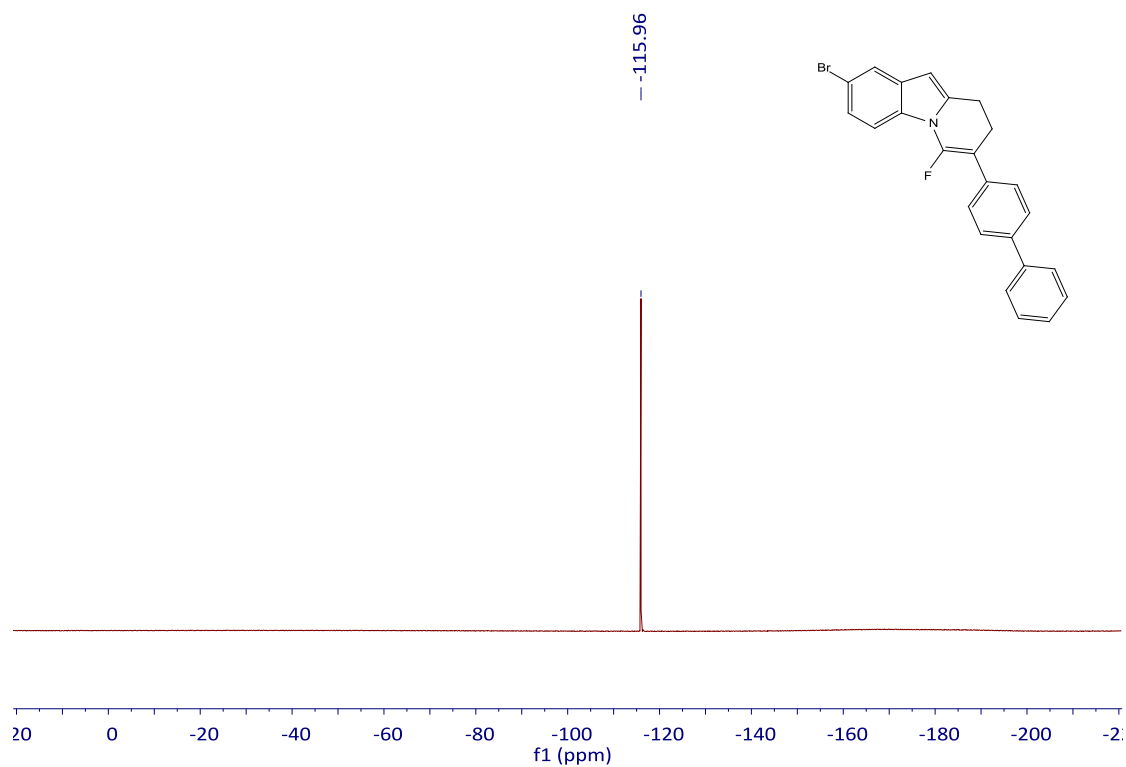


¹H NMR of **4x** (400 Hz, CDCl₃)

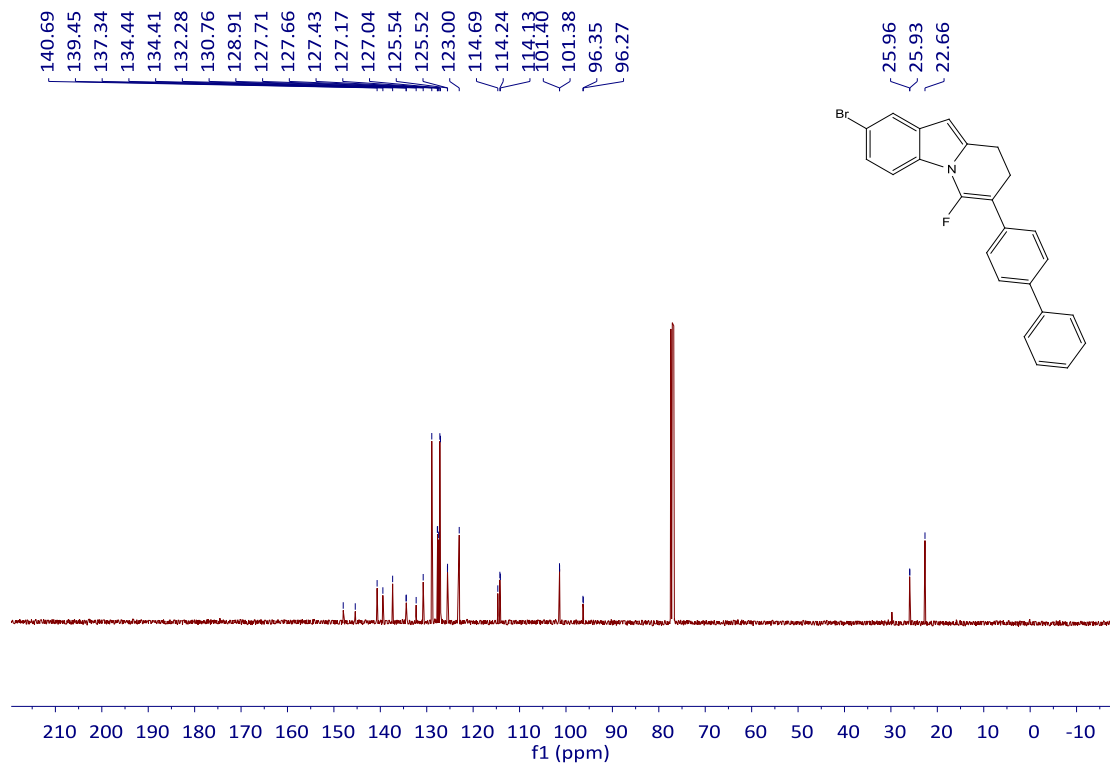




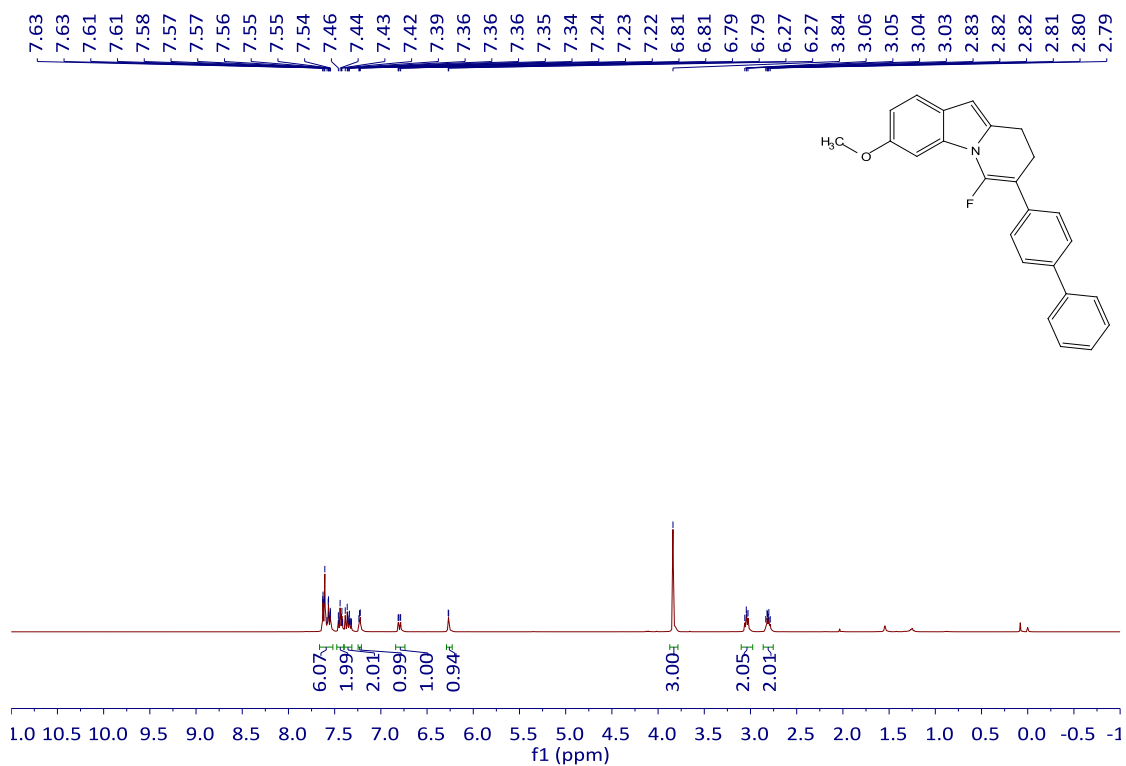
¹H NMR of **4y** (400 Hz, CDCl₃)



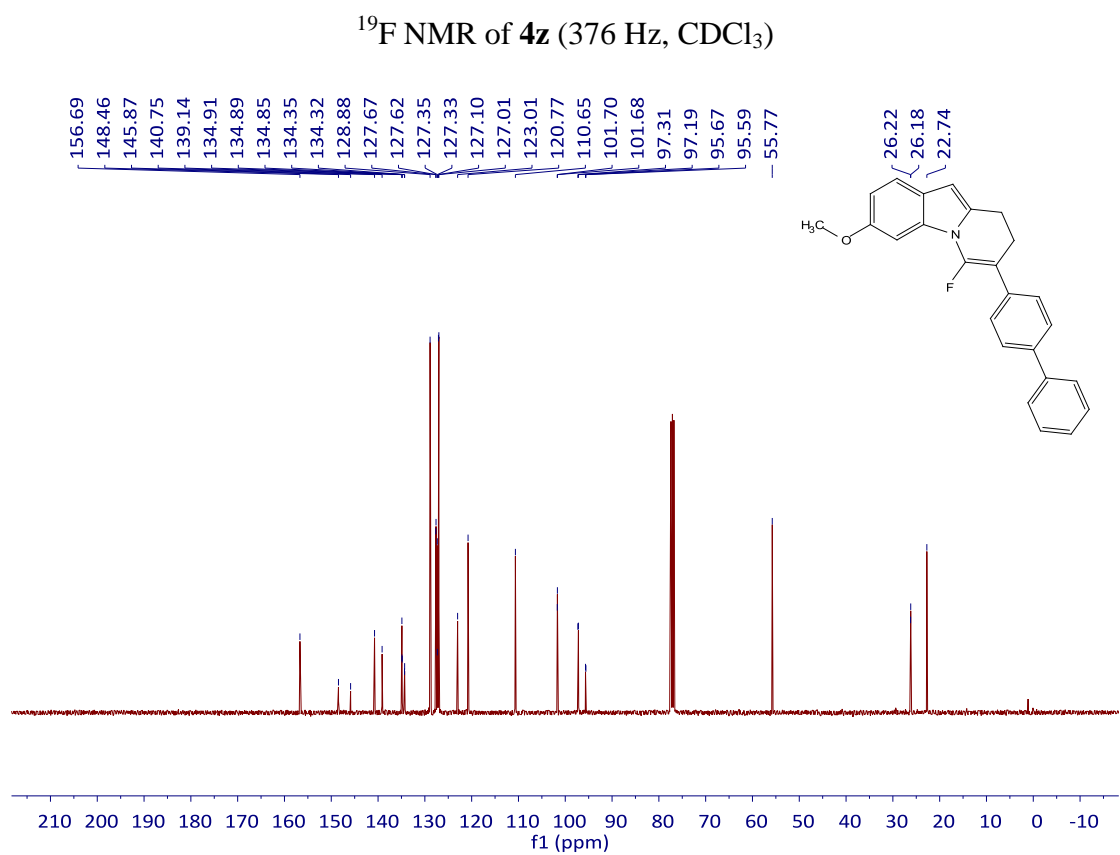
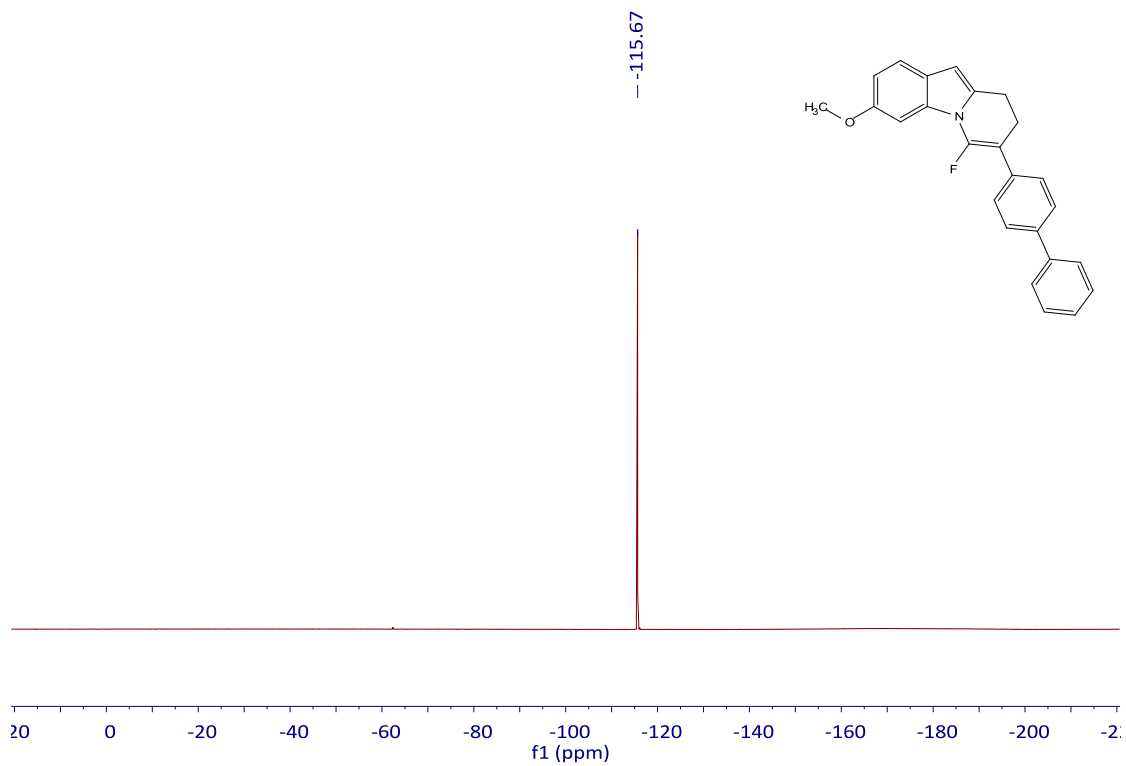
¹⁹F NMR of **4y** (376 Hz, CDCl₃)



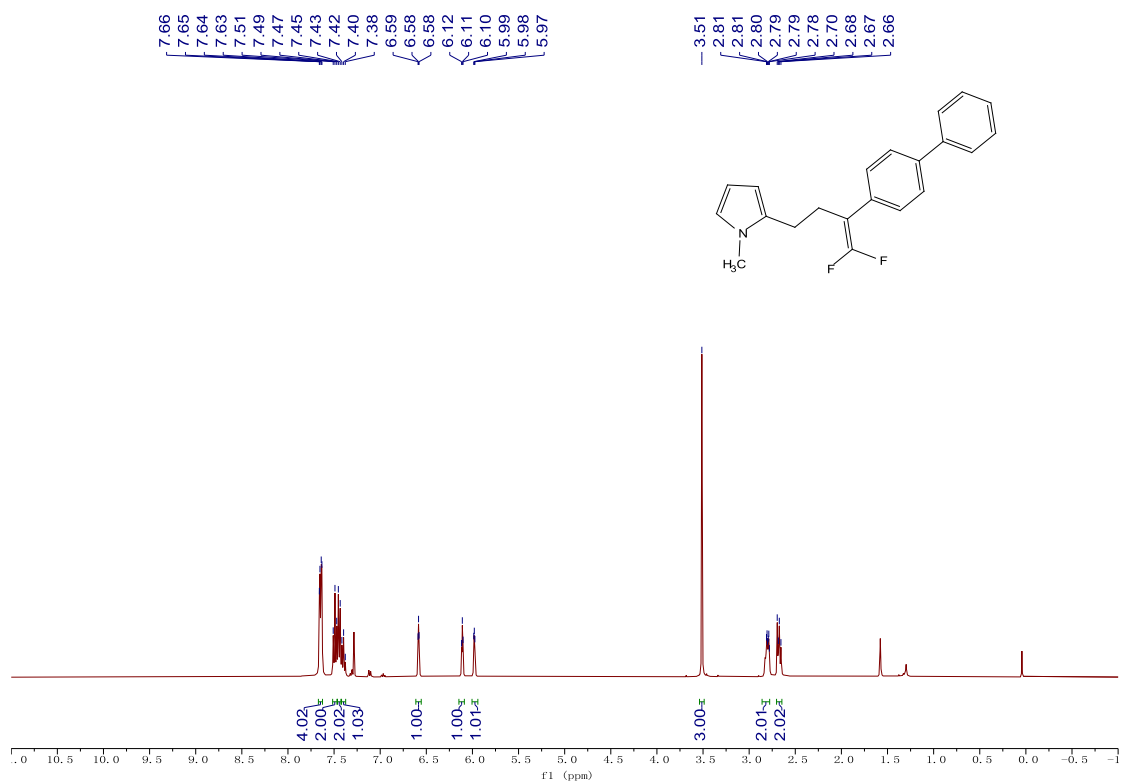
¹³C{¹H} NMR of **4y** (100 Hz, CDCl₃)



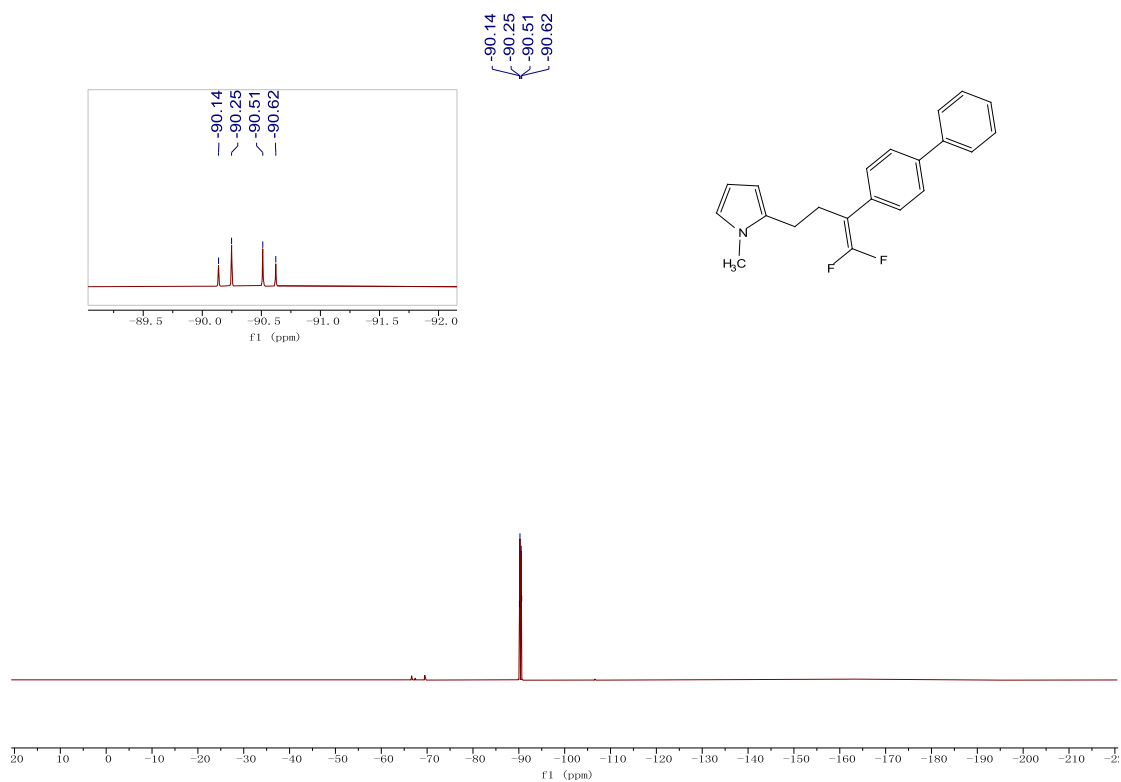
¹H NMR of **4z** (400 Hz, CDCl₃)



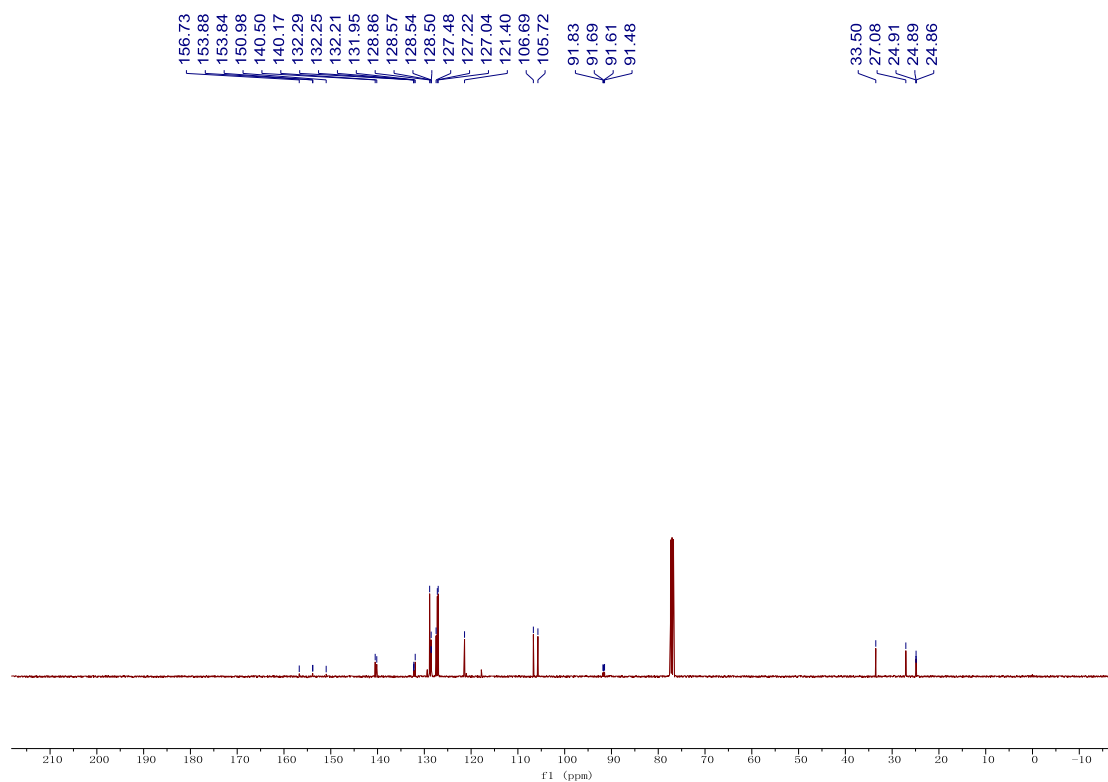
$^{13}\text{C}\{^1\text{H}\}$ NMR of **4z** (100 Hz, CDCl_3)



¹H NMR of **6** (400 Hz, CDCl₃)



¹⁹F NMR of **6** (376 Hz, CDCl₃)



$^{13}\text{C}\{^1\text{H}\}$ NMR of **6** (100 Hz, CDCl_3)