

Supporting Information

Electrochemical Radical Tandem Difluoroethylation/ Cyclization of Unsaturated Amides to Access MeCF₂- Featured Indolo/Benzoimidazo [2,1-a]Isoquinolin-6(5H)-ones

Yunfei Tian ^{1,*}, Dongyu Guo ², Luping Zheng ¹, Shaolu Yang ¹, Ningning Zhang ¹, Weijun Fu ¹ and Zejiang Li ²

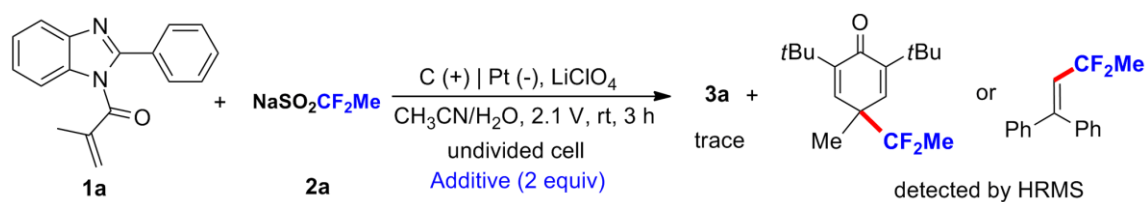
¹Key Laboratory of Function-Oriented Porous Materials of Henan Province, College of Chemistry and Chemical Engineering, Luoyang Normal University, Luoyang 471934, China; zhen-glp0213@163.com (L.Z.); 13525275309@163.com (S.Y.); n18736243401@126.com (N.Z.); wjfu@lynu.edu.cn (W.F.)

²Key Laboratory of Medicinal Chemistry and Molecular Diagnosis of the Ministry of Education, State Key Laboratory of New Pharmaceutical Preparations and Excipients, Key Laboratory of Chemical Biology of Hebei Province, College of Chemistry & Materials Science, Hebei University, Baoding 071002, China; 18712762730@163.com (D.G.); lizejiang898@126.com (Z.L.)

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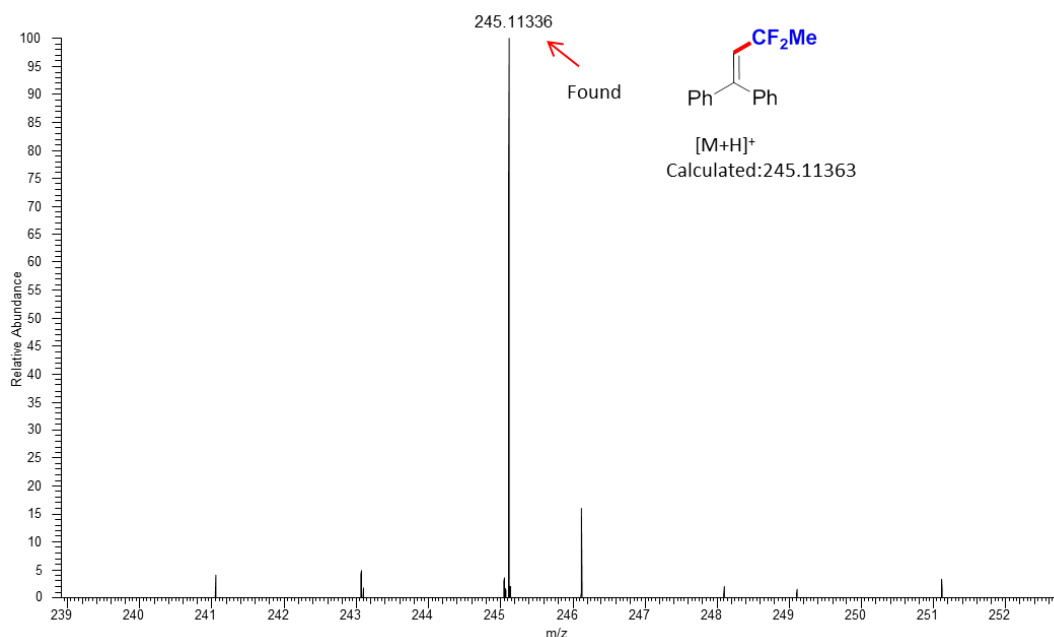
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1. Radical capturing experiments



To a 20 mL test tube with a stir bar was charged with, 2-arylbenzimidazoles (1 equiv., 0.2 mmol), $\text{MeCF}_2\text{SO}_2\text{Na}$, or sodium cyclopropyldifluoromethylsulfinate (3 equiv., 0.6 mmol), LiClO_4 (0.3 M), MeCN (4.5 mL), H_2O (1.5 mL). The tube was equipped with a carbon plate (10 mm * 10 mm * 3 mm) as the anode and a platinum plate (10 mm × 10 mm × 0.2 mm) as the cathode. The reaction mixture was electrolyzed in an undivided cell at room temperature under a constant voltage of 2.1 V for 3 h. Upon completion, the mixture was extracted with EtOAc (10 mL × 3). The combined organic phases were dried over Na_2SO_4 and condensed under vacuum. The difluoroethylation of 2-arylbenzimidazoles was almost prohibited and the adduct products were detected by HRMS analysis (Figure S1)

51 #15 RT: 0.18 AV: 1 NL: 3.97E6
T: FTMS [1.1] + p APCI corona Full ms [100.00-1000.00]



52_230915164904#26 RT: 0.30 AV:1 NL: 2.76E6
T: FTMS [1,2] - p APCI corona Full ms [100.00-1000.00]

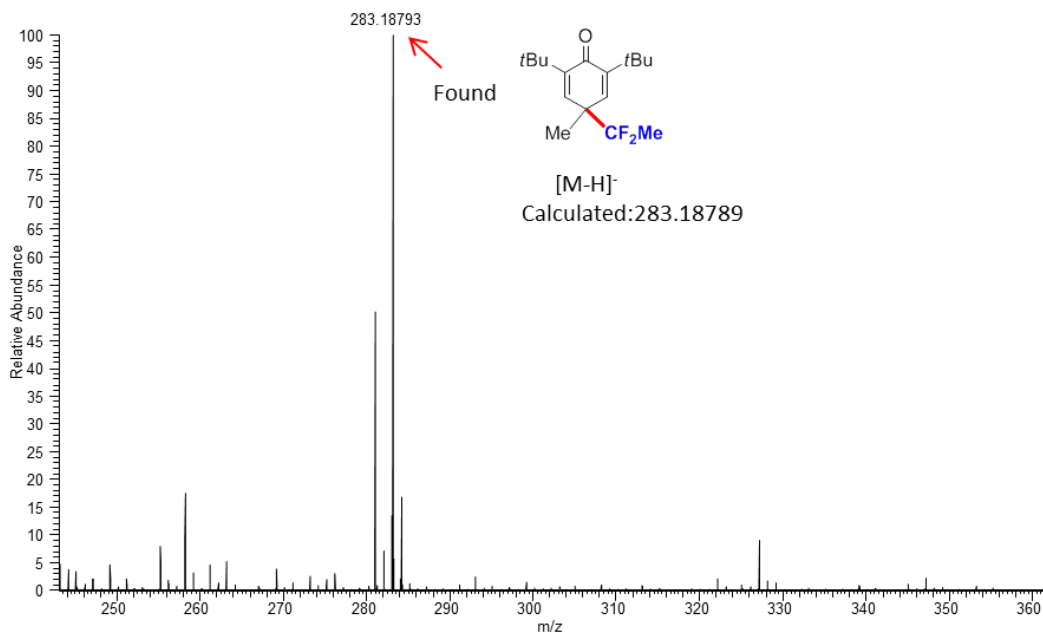


Figure S1. HRMS analysis of adduct products

2. Cyclic voltammetry experiments

The cyclic voltammograms experiments were performed in a three-electrode system with an electrochemical workstation (CHI660E, Shanghai, China) under air at room temperature. A glassy carbon electrode working electrode, a platinum wire counter electrode, and an Ag/AgNO₃ reference electrode were used. The scan rate was 50 mV/s, from 0 V to 2 V. 5 mM analyte and 0.1 M LiClO₄ was dissolved in the mixture of acetonitrile and H₂O.

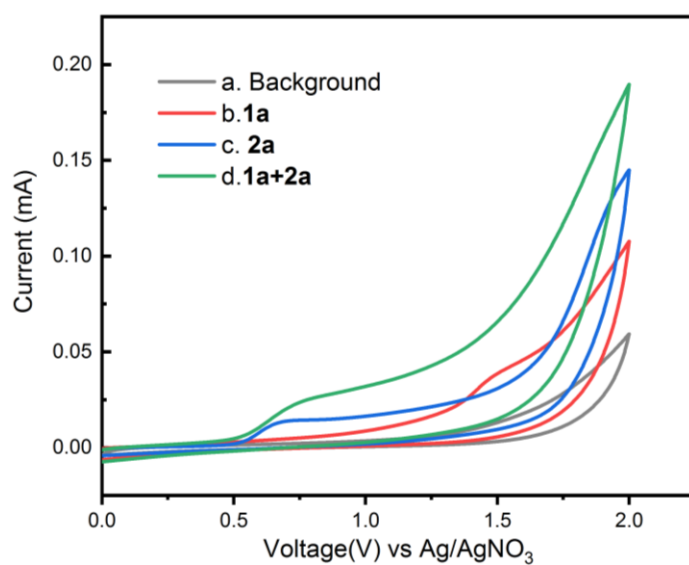
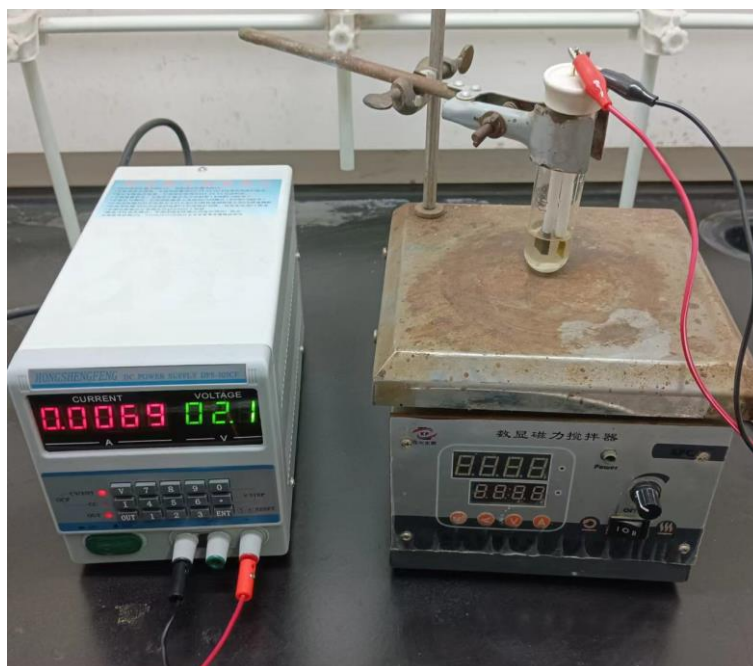


Figure S2. Cyclic voltammograms of substrates: (a) Background (0.1 M LiClO₄ in CH₃CN/H₂O (10/1,

V/V)), (b) **1a** (5 mM), (c) **2a** (5 mM), (d) **1a** (5 mM)+**2a** (5 mM).

3. Photo of of the electrochemical setup



4. Crystallographic details of product **3m**

(1) Product **3m** was solved with 1 mL dichloromethane in a sample bottle. Then 2 mL petroleum ether was added to the above mixture. Finally, the sample bottle was sealed and placed in a dark cabinet. The crystal was precipitated via volatilizing after several days.

(2) A single crystal of $C_{19}H_{15}BrF_2N_2O$ [Product **3m**] was offered as follows: A proper crystal was selected and detected on an Oxford Diffraction Gemini. The crystal stayed at 293.0 K during data collection. With the assistance of Shelxtl, the structure was solved with the XShell structure solution program using Charge Flipping, and it was refined with the SHELXL [1] refinement package using Least Squares minimization. Finally, crystal data and structure refinement parameters of product **3m** are described as depicted in Table S1. CCDC No. 2303467. This material is available free of charge via the Internet at <http://www.ccdc.cam.ac.uk/>.

Table S1. Crystal data of compound **3m**.

Empirical formula	$C_{19}H_{15}BrF_2N_2O$
Formula weight	405.24
Temperature/K	293(2)

Crystal system	orthorhombic
Space group	Pbca
$a/\text{\AA}$	13.5964(9)
$b/\text{\AA}$	13.6099(7)
$c/\text{\AA}$	18.1837(8)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
Volume/ \AA^3	3364.8(3)
Z	8
$\rho_{\text{calc}} (\text{g cm}^{-3})$	1.600
$\mu (\text{mm}^{-1})$	2.473
$F(000)$	1632.0
Crystal size/ mm^3	$0.29 \times 0.28 \times 0.23$
Radiation	Mo K α ($\lambda = 0.71073$)
2θ range for data collection/ $^\circ$	6.7 to 58.334
Index ranges	$-17 \leq h \leq 17, -15 \leq k \leq 17, -24 \leq l \leq 23$
Reflections collected	17858
Independent reflections	4072 [Rint = 0.0650, Rsigma = 0.0880]
Data/restraints/parameters	4072/0/228
Goodness-of-fit on F^2	1.016
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0590, wR_2 = 0.1029$
Final R indexes [all data]	$R_1 = 0.1513, wR_2 = 0.1314$
Largest diff. peak/hole / e \AA^{-3}	0.40/-0.39
CCDC	2303467
Displacement ellipsoids are drawn at the 50% probability level	

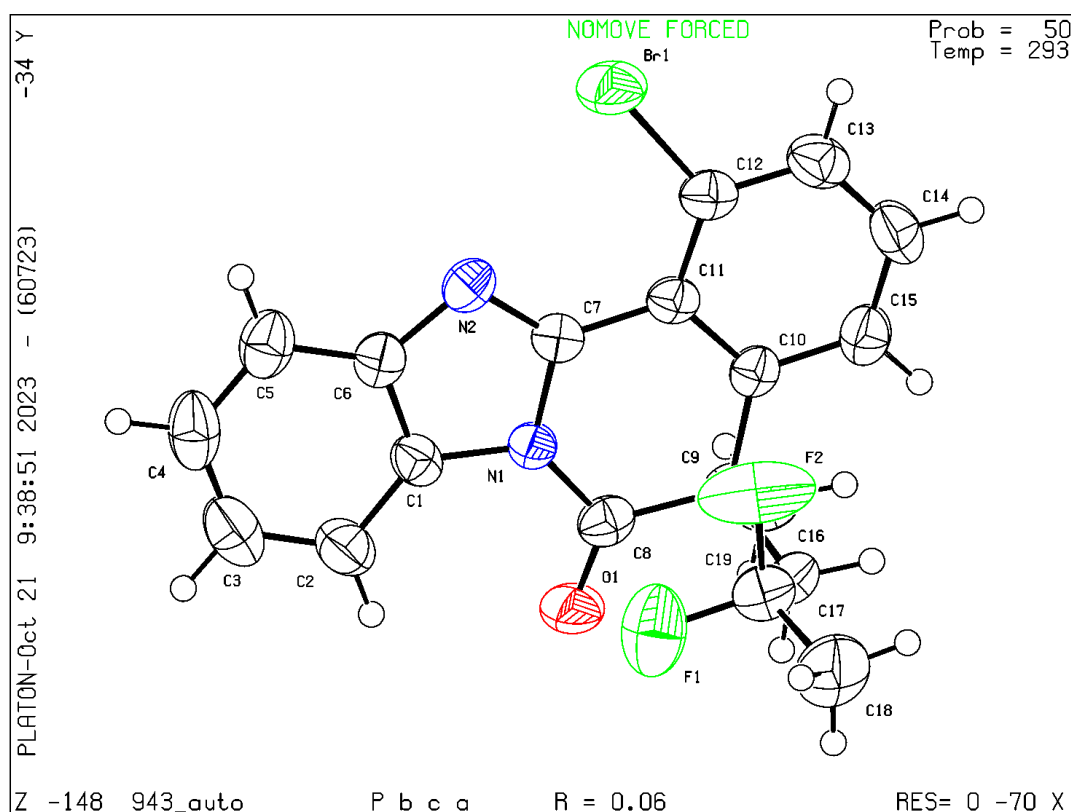


Fig. S3 Structure of product **3m**

5. Crystallographic details of product **5i**

(1) Product **5i** was solved with 1 mL of dichloromethane in a sample bottle. Then 2 mL petroleum ether was added to the above mixture. Finally, the sample bottle was sealed and placed in a dark cabinet. The crystal was precipitated via volatilizing after several days.

(2) A single crystal of $C_{23}H_{20}ClF_2NO$ [Product **5i**] was offered as follows: A proper crystal was selected and detected on a 'D8 VENTURE' diffractometer. The crystal stayed at 150.0 K during data collection. With the assistance of Shelxtl, the structure was solved with the XShell structure solution program using Charge Flipping, and it was refined with the SHELXL [1] refinement package using Least Squares minimization. Finally, crystal data and structure refinement parameters of product **5i** are described as depicted in Table S2. CCDC No. 2307007. This material is available free of charge via the Internet at <http://www.ccdc.cam.ac.uk/>.

Table S2. Crystal data of compound **5i**.

Empirical formula	$C_{23}H_{20}ClF_2NO$
Formula weight	399.85

Temperature/K	150
Crystal system	monoclinic
Space group	P2 ₁ /c
<i>a</i> /Å	9.1778(4)
<i>b</i> /Å	10.0556(5)
<i>c</i> /Å	20.7235(11)
α /°	90
β /°	94.132(2)
γ /°	90
Volume/Å ³	1907.57(16)
<i>Z</i>	4
ρ_{calc} (g cm ⁻³)	1.392
μ (mm ⁻¹)	0.233
<i>F</i> (000)	832.0
Crystal size/mm ³	0.15 × 0.08 × 0.06
Radiation	Mo K α (λ = 0.71073)
2 θ range for data collection/°	3.942 to 52.848
Index ranges	-11 ≤ <i>h</i> ≤ 11, -12 ≤ <i>k</i> ≤ 12, -25 ≤ <i>l</i> ≤ 22
Reflections collected	15768
Independent reflections	3873 [R _{int} = 0.0667, R _{sigma} = 0.0561]
Data/restraints/parameters	3873/0/255
Goodness-of-fit on <i>F</i> ²	1.037
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	R1 = 0.0460, wR2 = 0.1122
Final <i>R</i> indexes [all data]	R1 = 0.0596, wR2 = 0.1214
Largest diff. peak/hole / e Å ⁻³	0.30/-0.31
CCDC	2307007
Displacement ellipsoids are drawn at the 50% probability level	

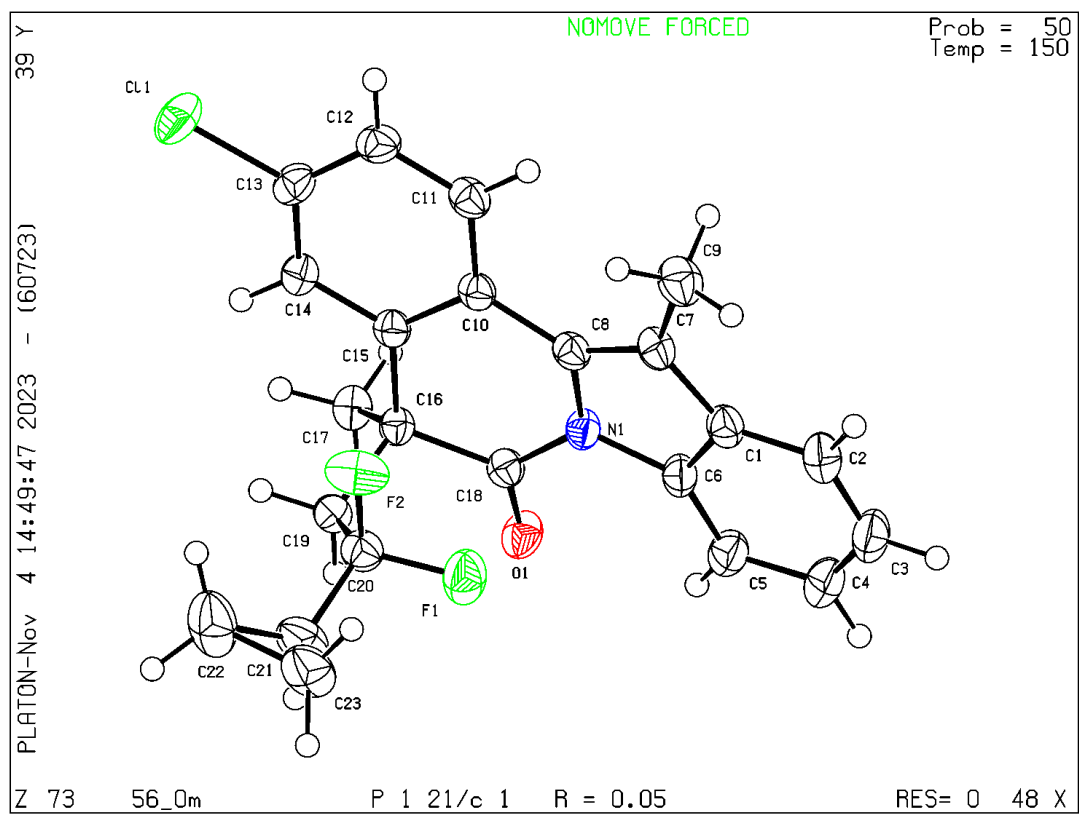
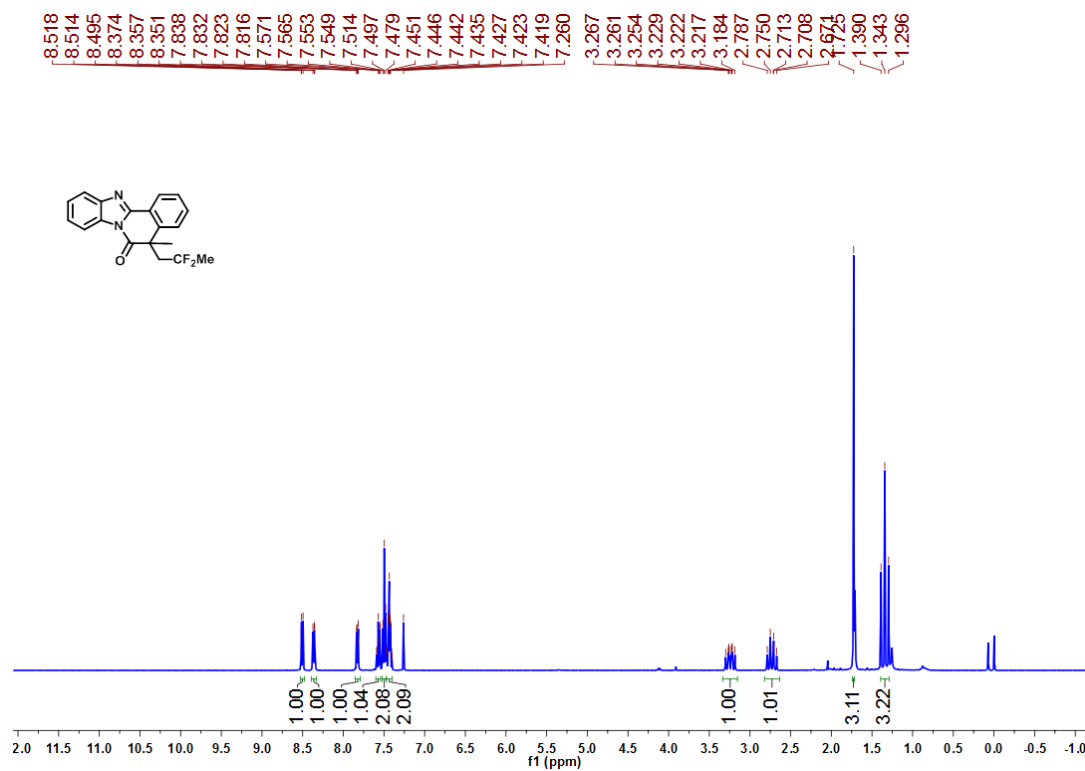


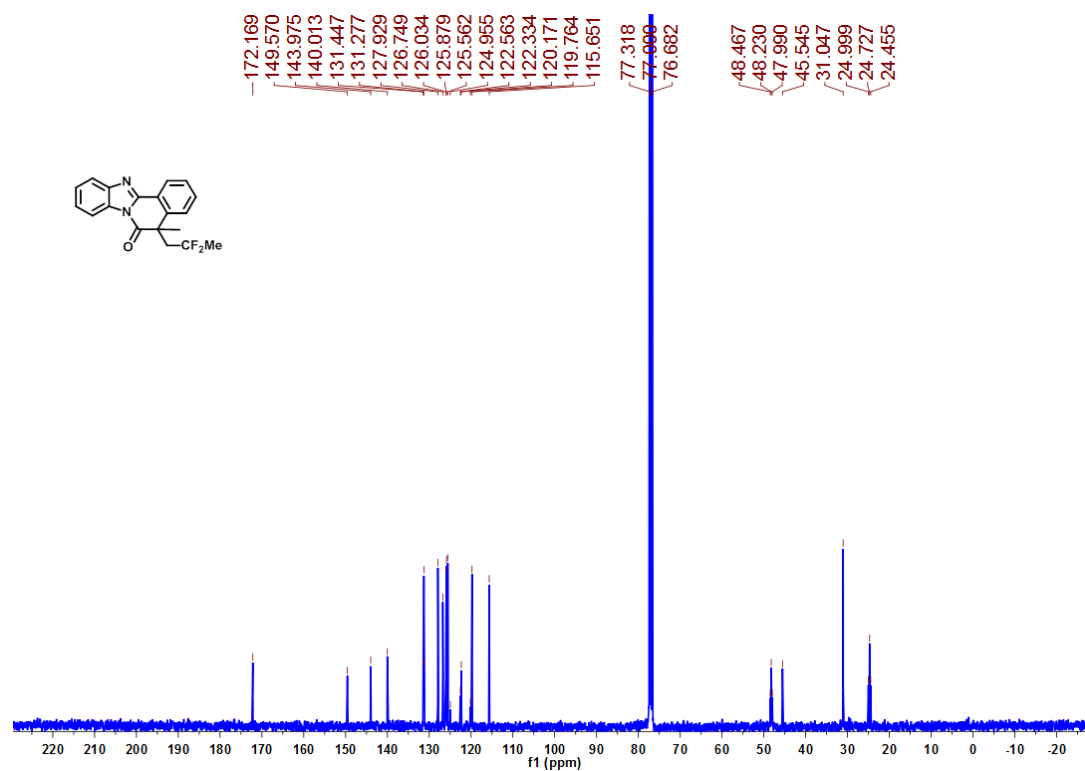
Fig. S4 Structure of product **5i**

6. Copies of the ^1H NMR, ^{13}C NMR and ^{19}F NMR

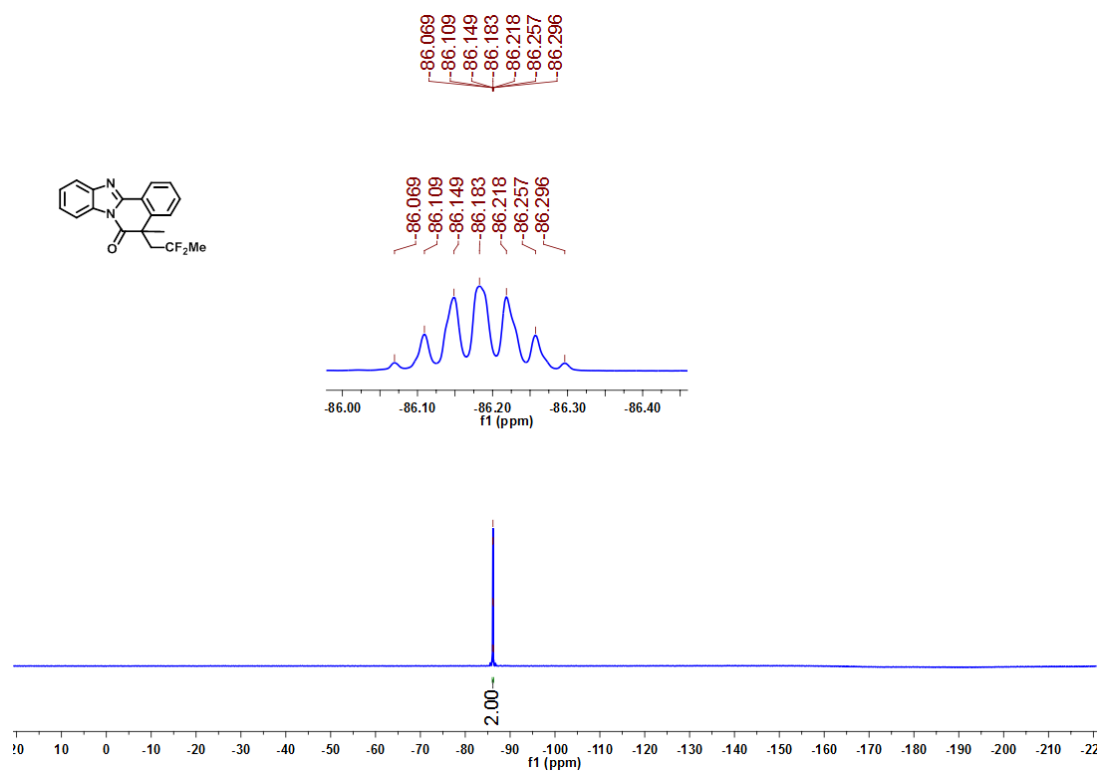
3a- ^1H NMR (400 MHz, CDCl_3)



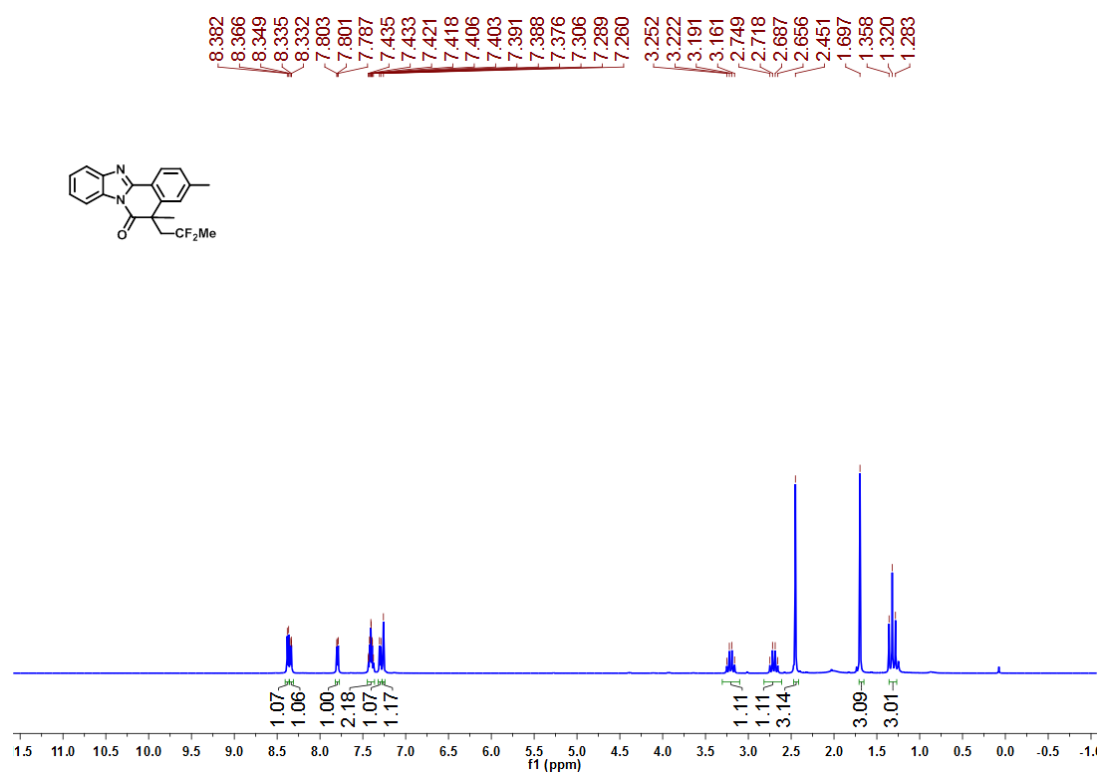
3a- $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3)



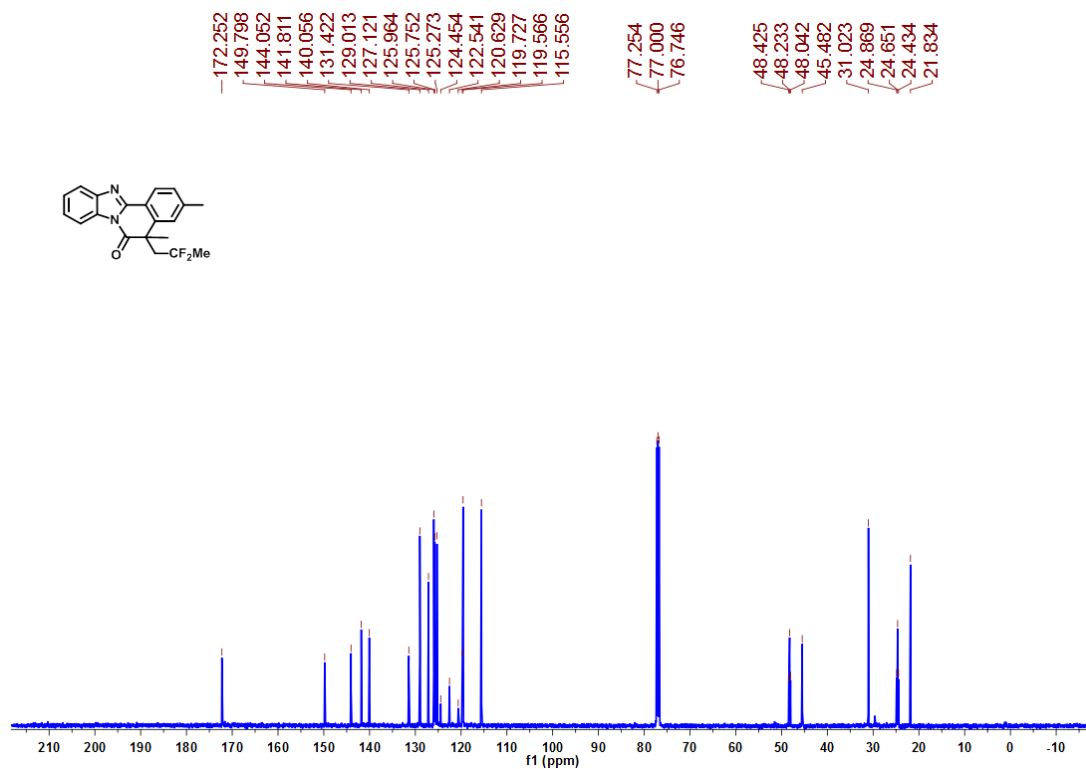
3a-¹⁹F NMR (471 MHz, CDCl₃)



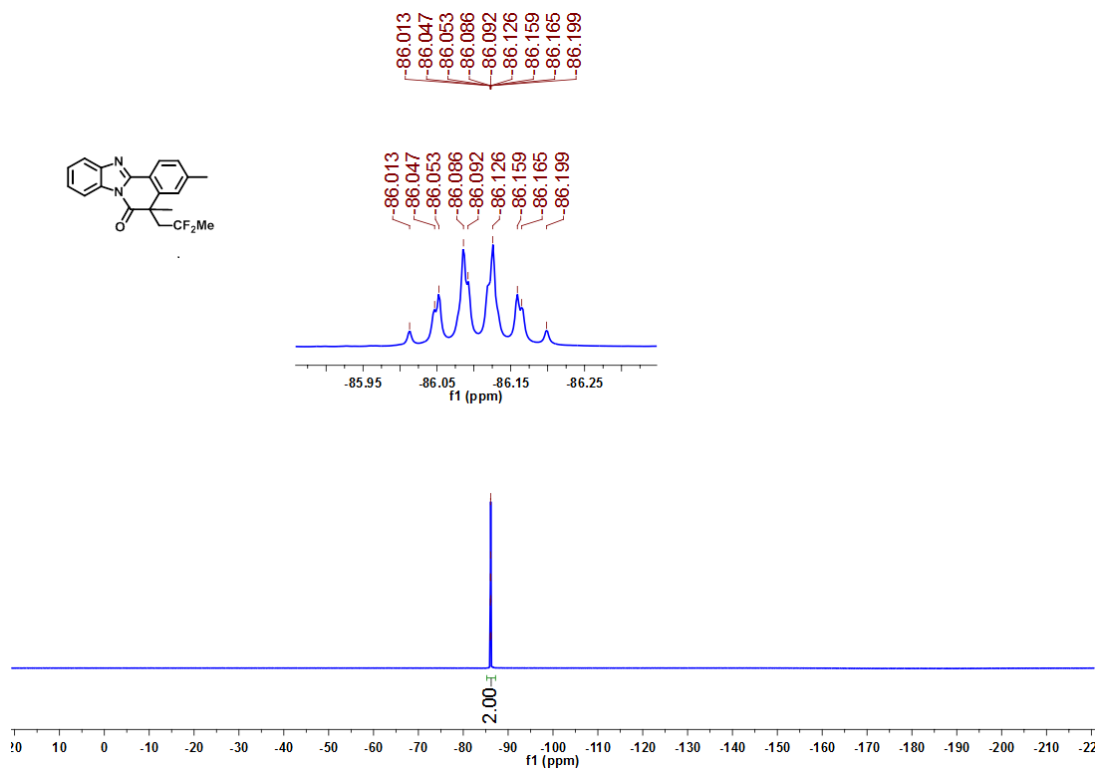
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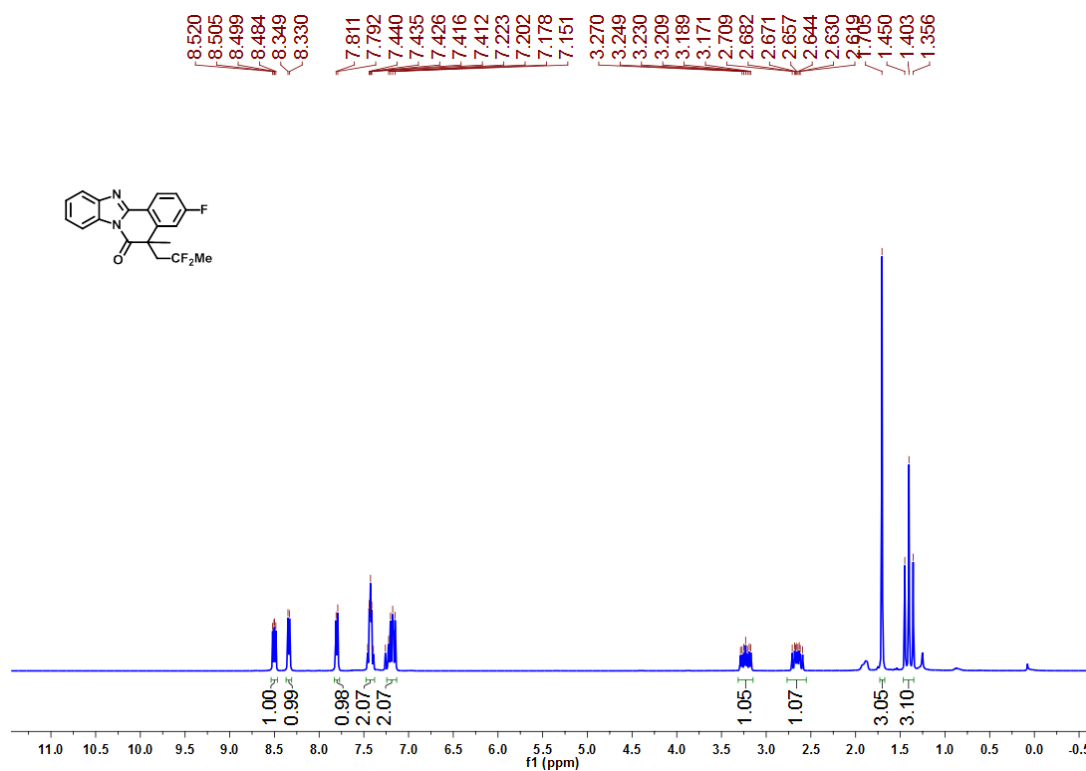
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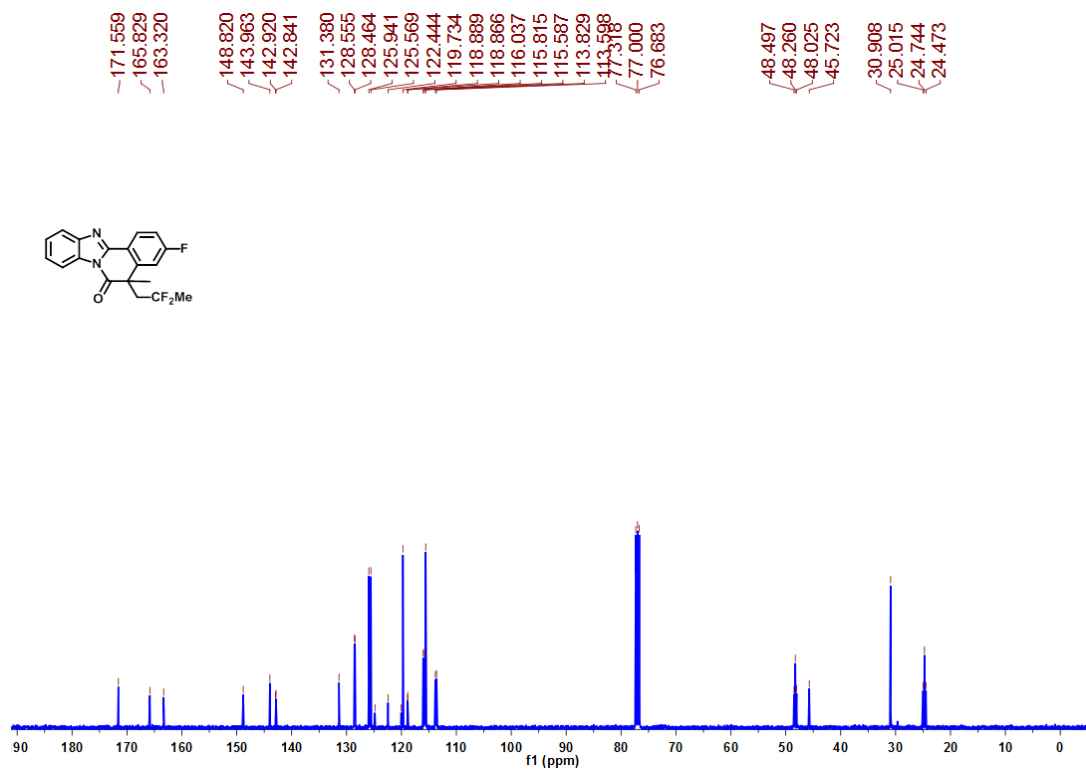
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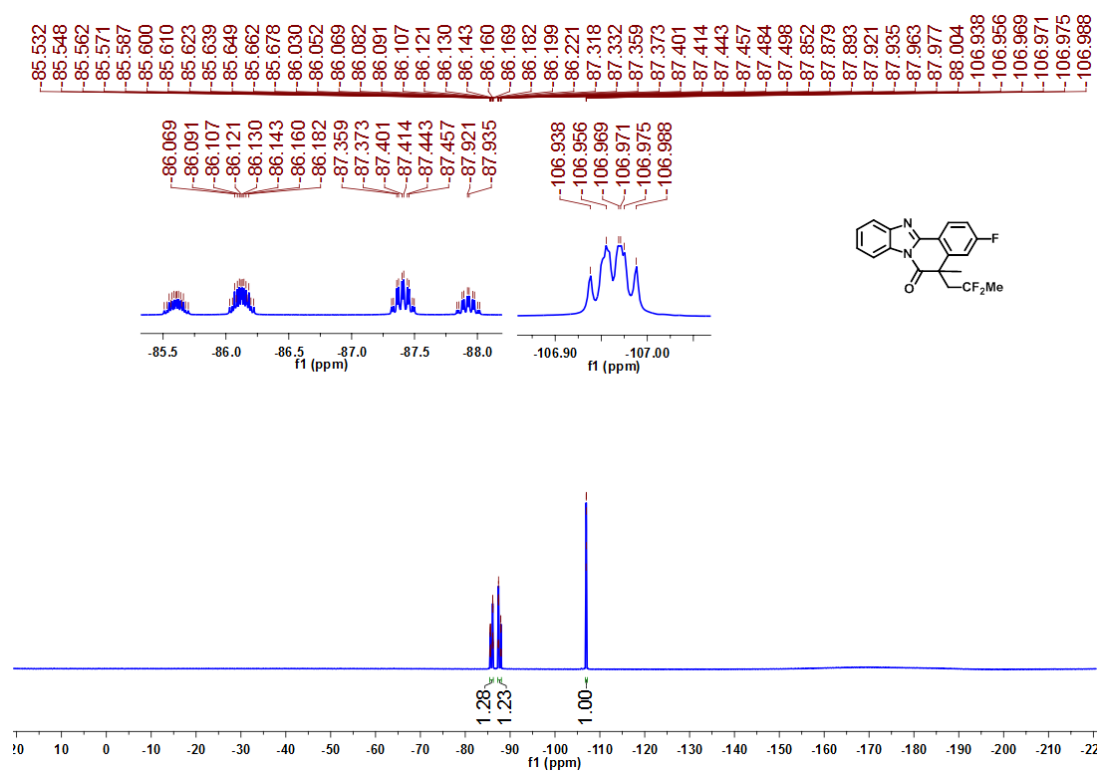
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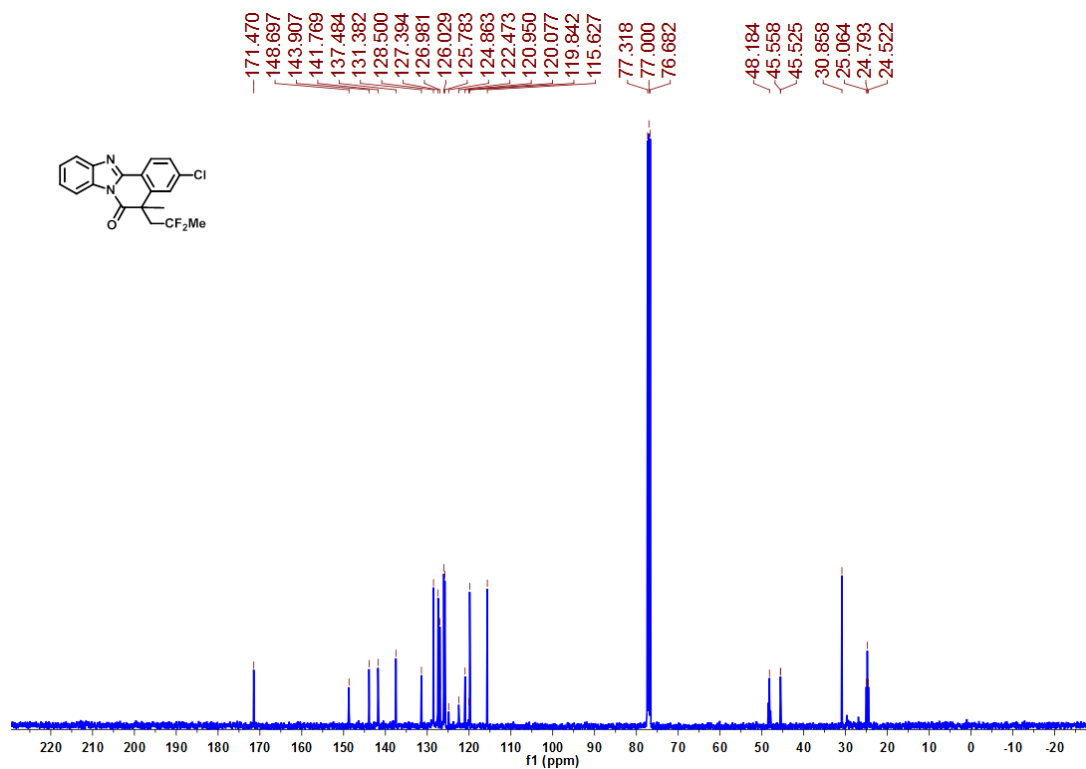
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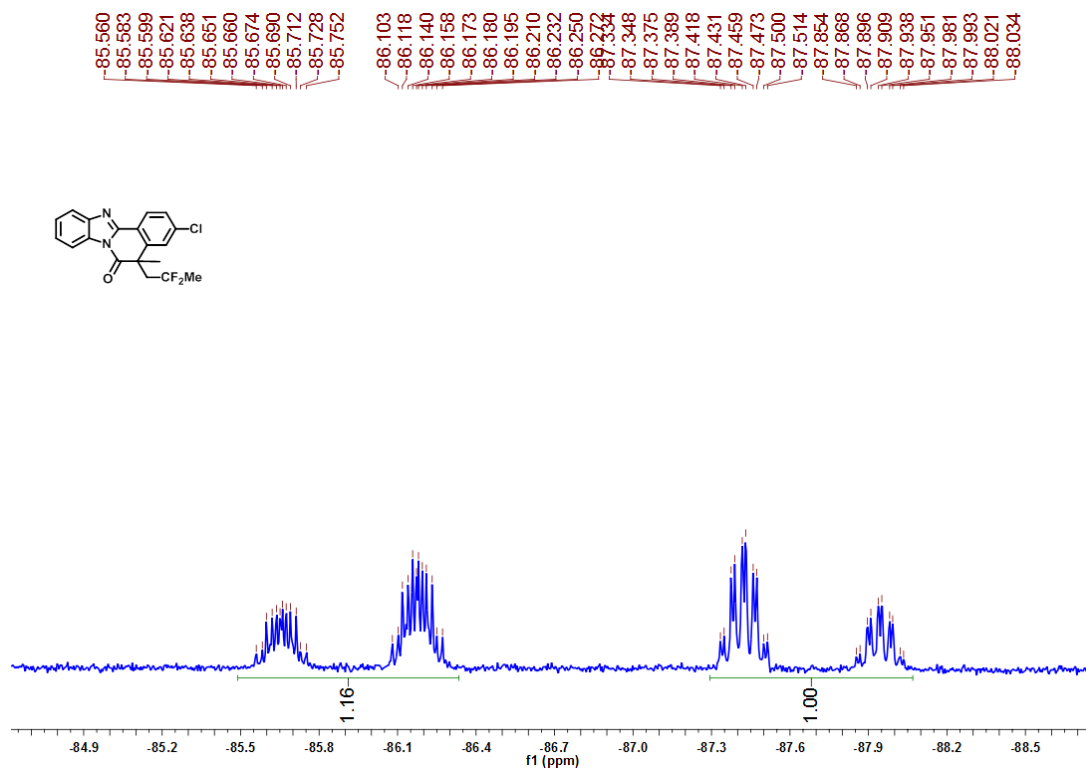
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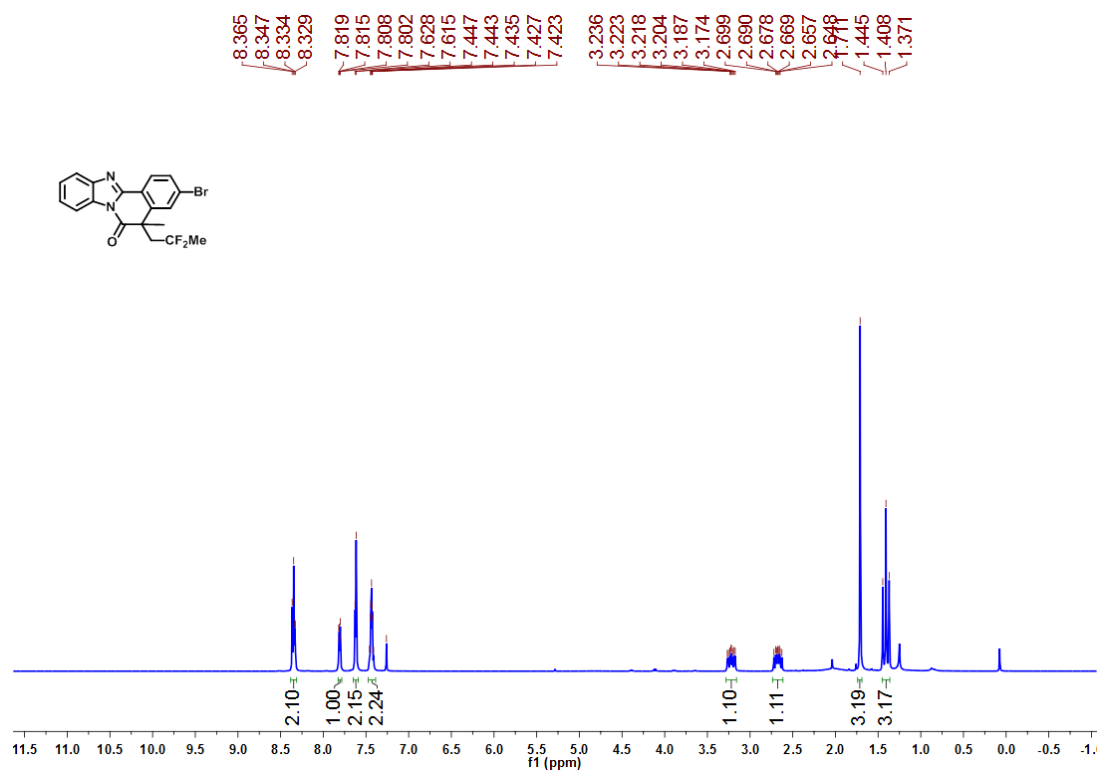
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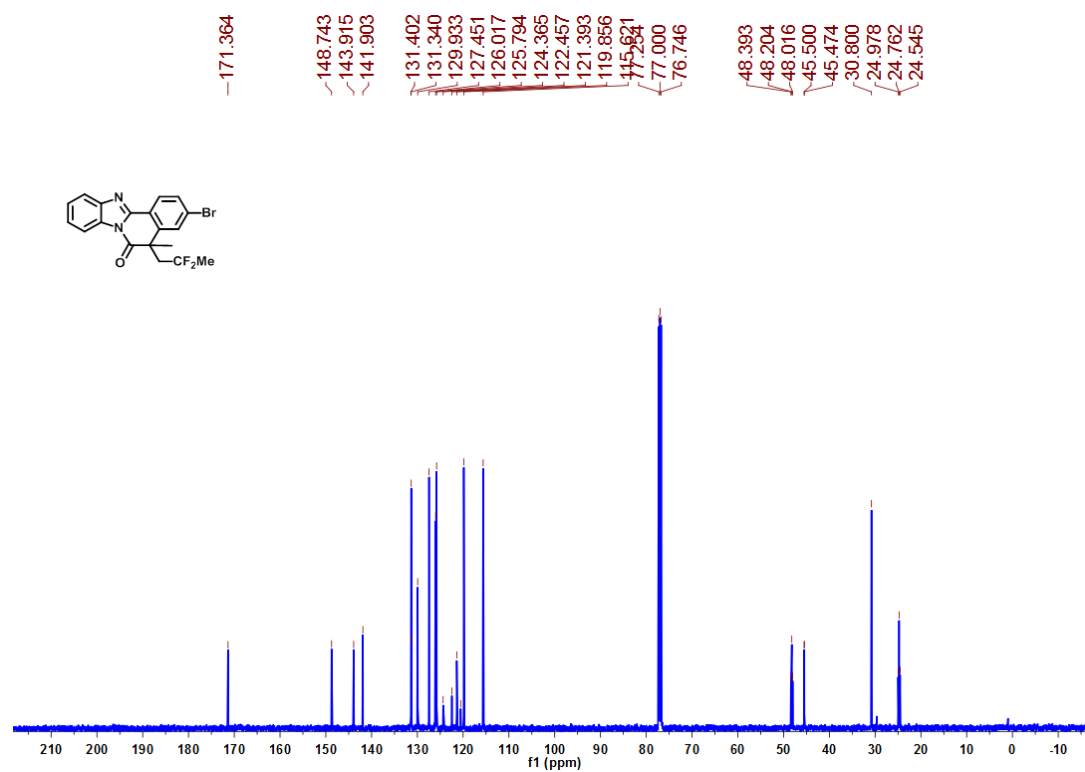
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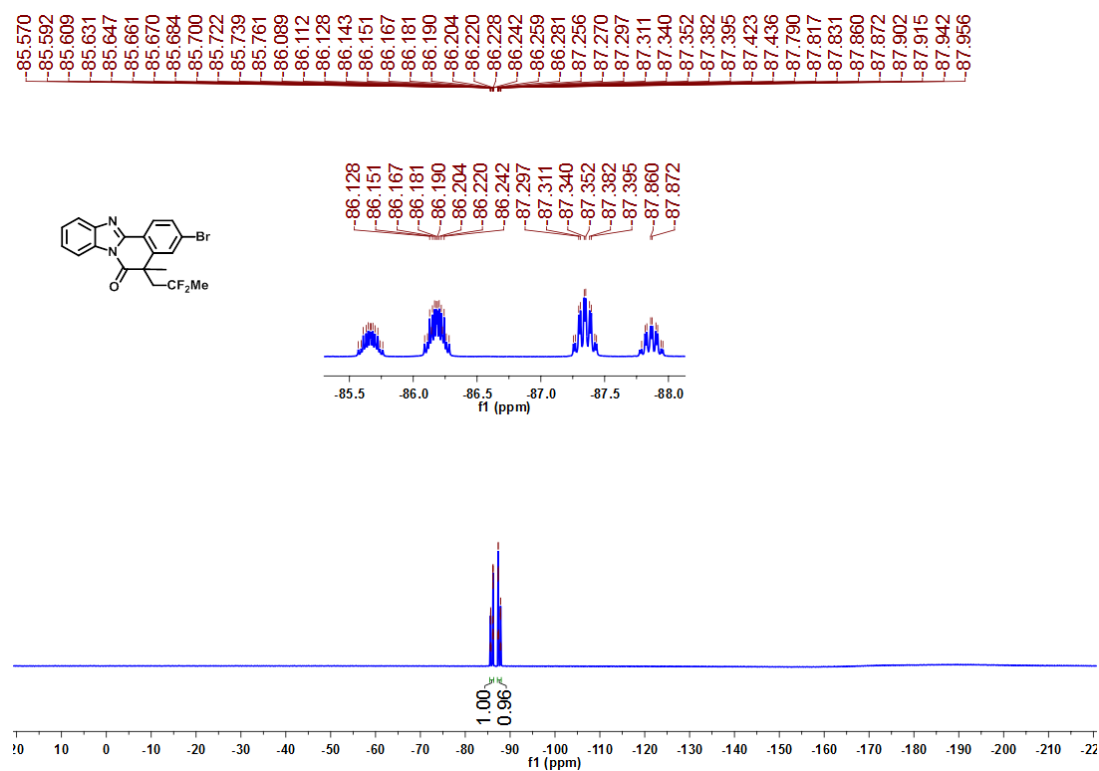
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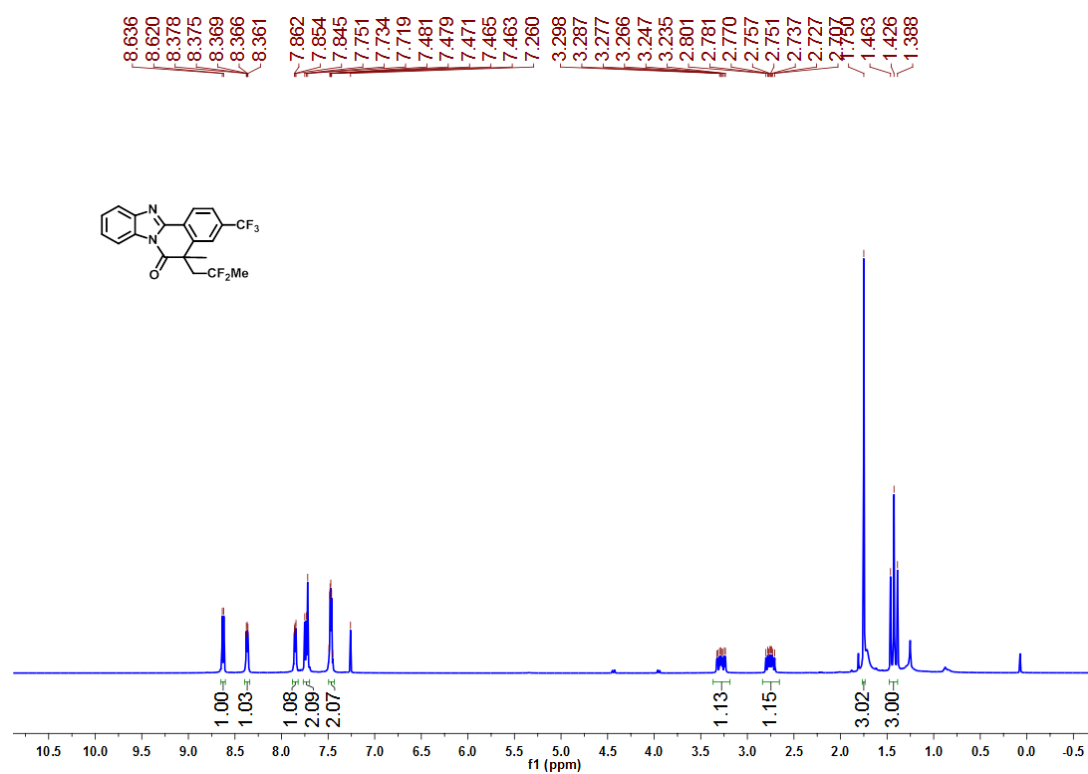
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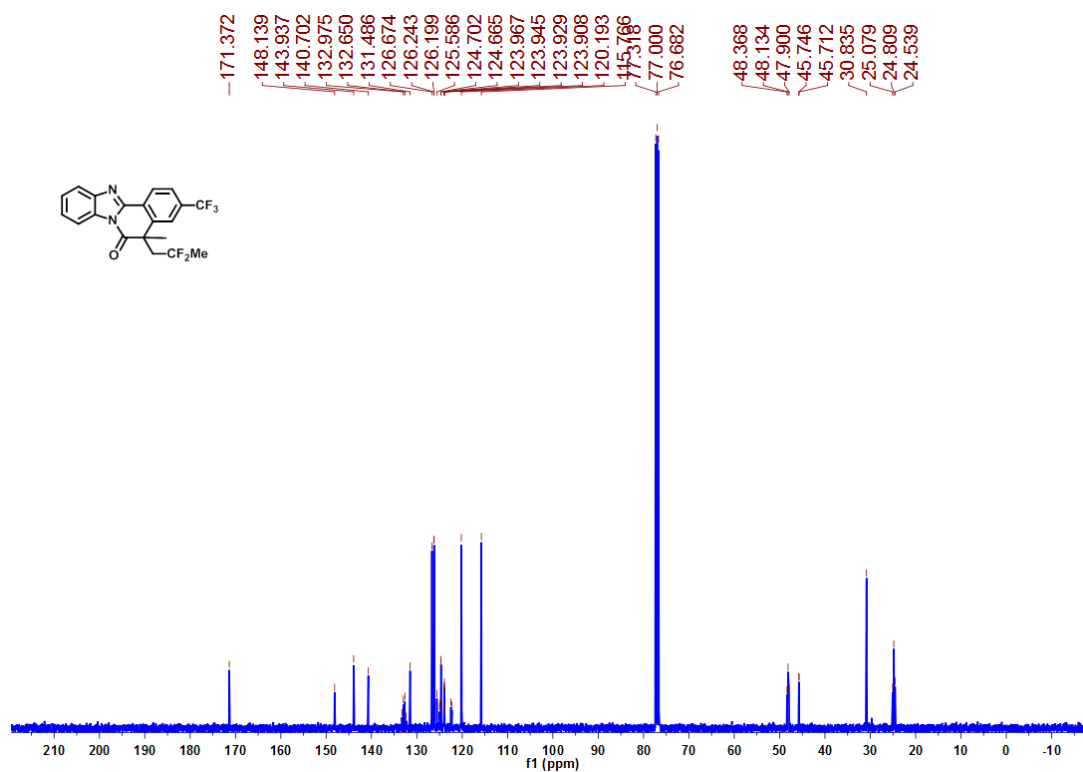
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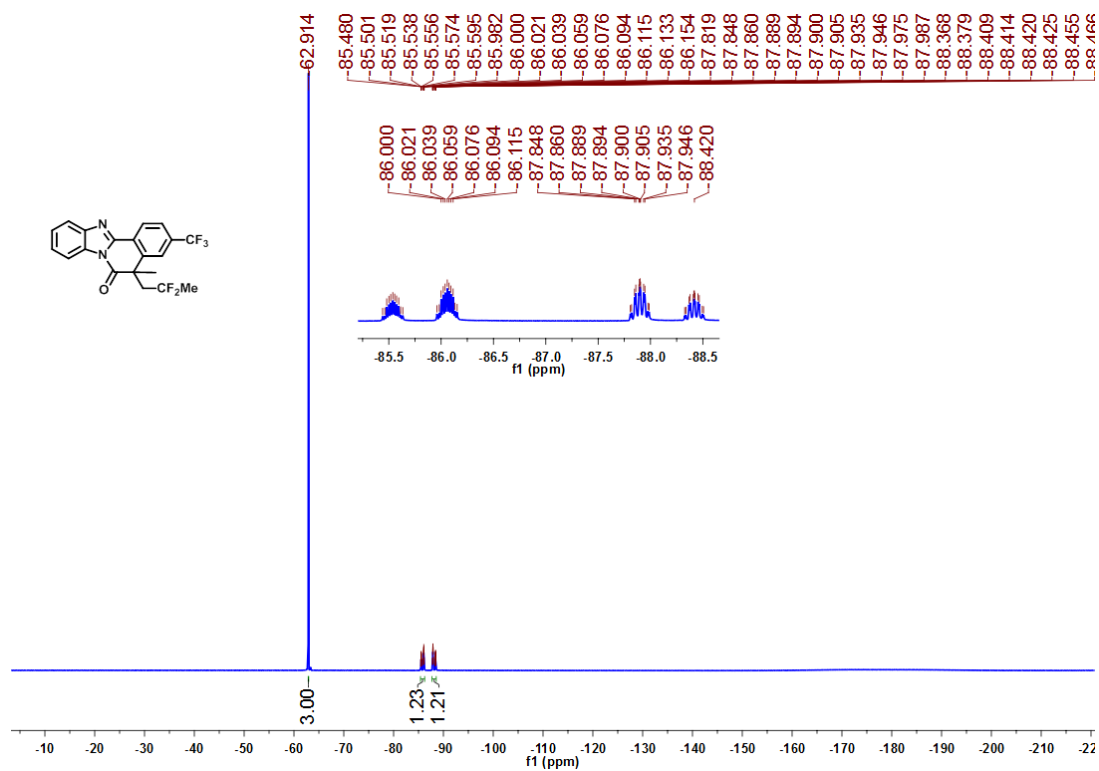
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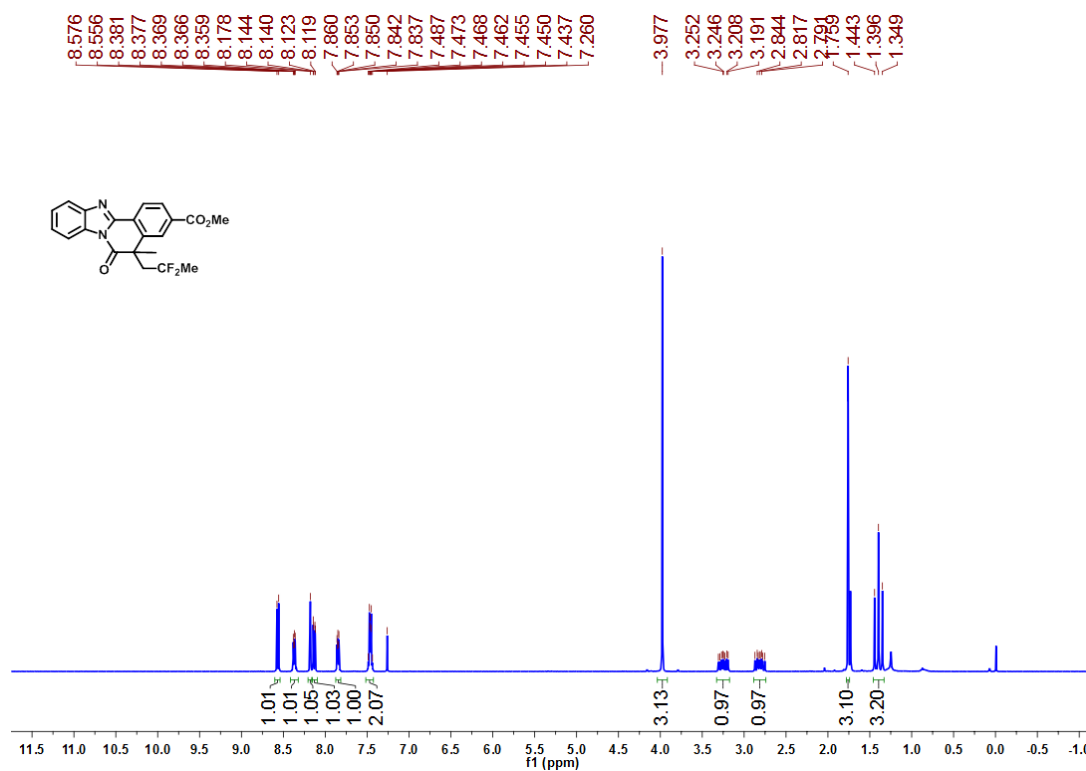
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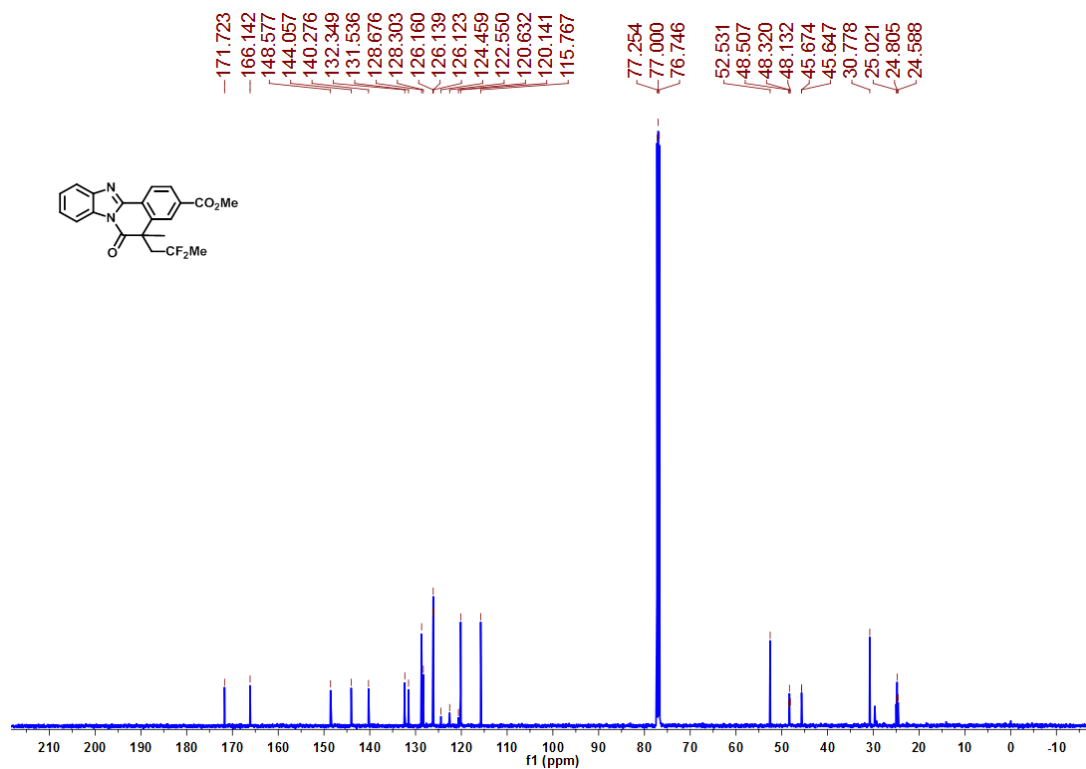
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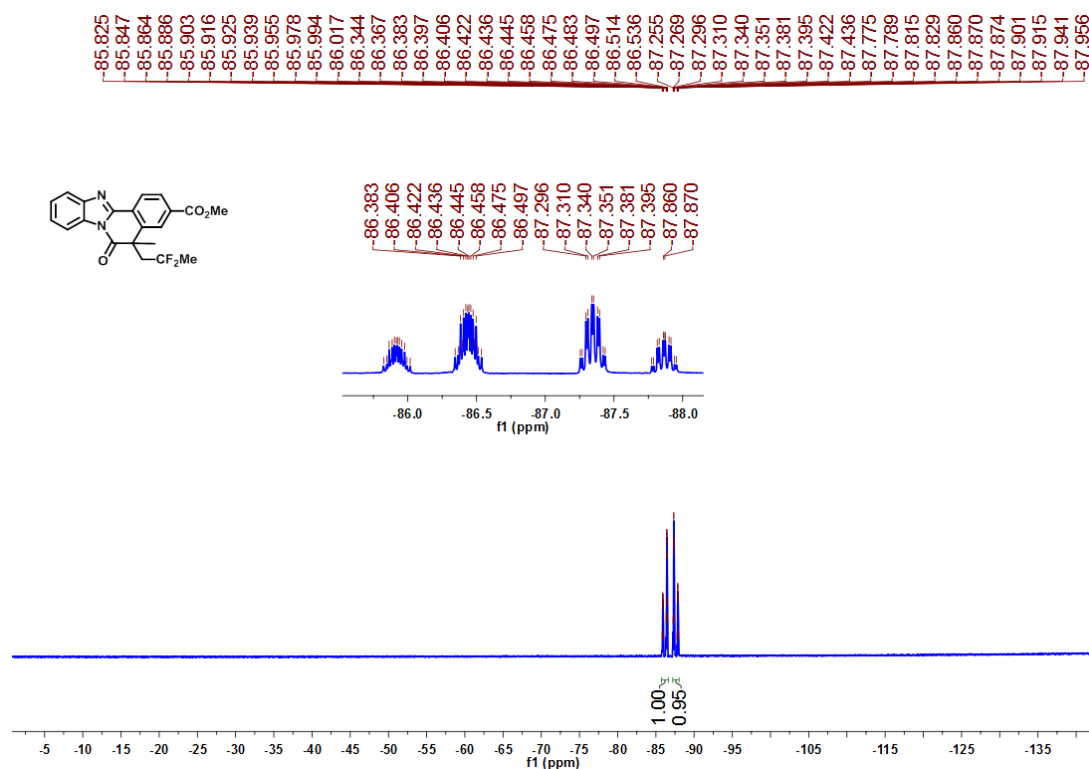
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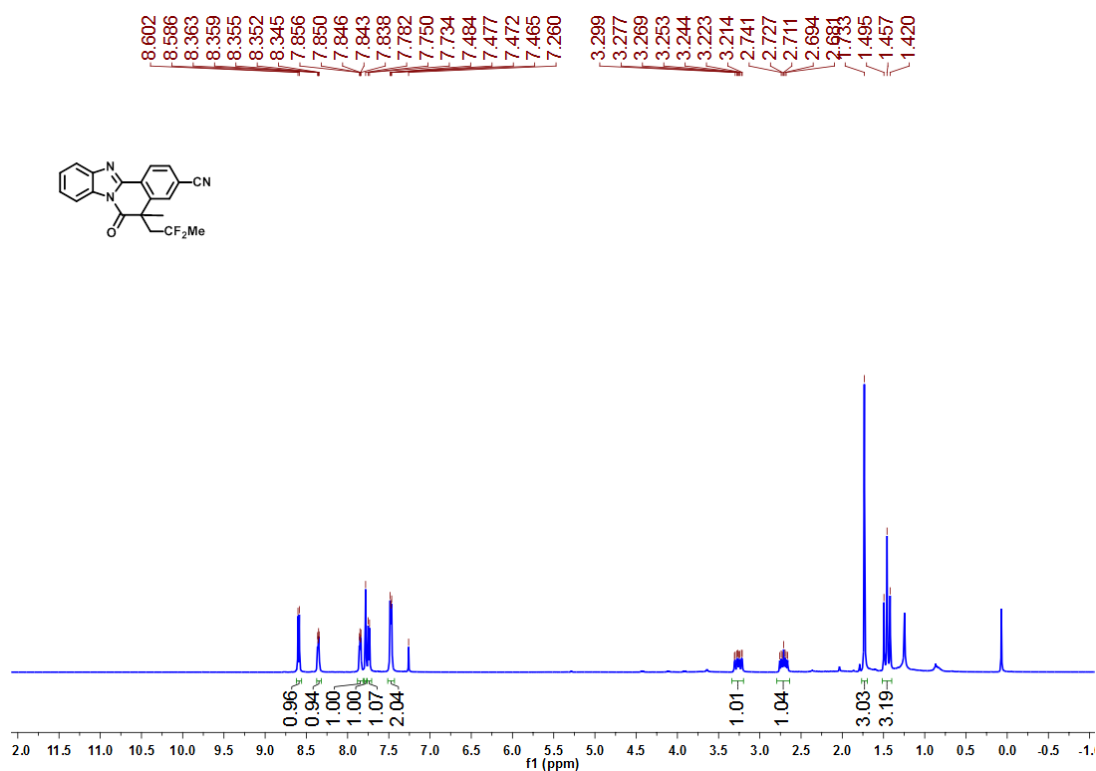
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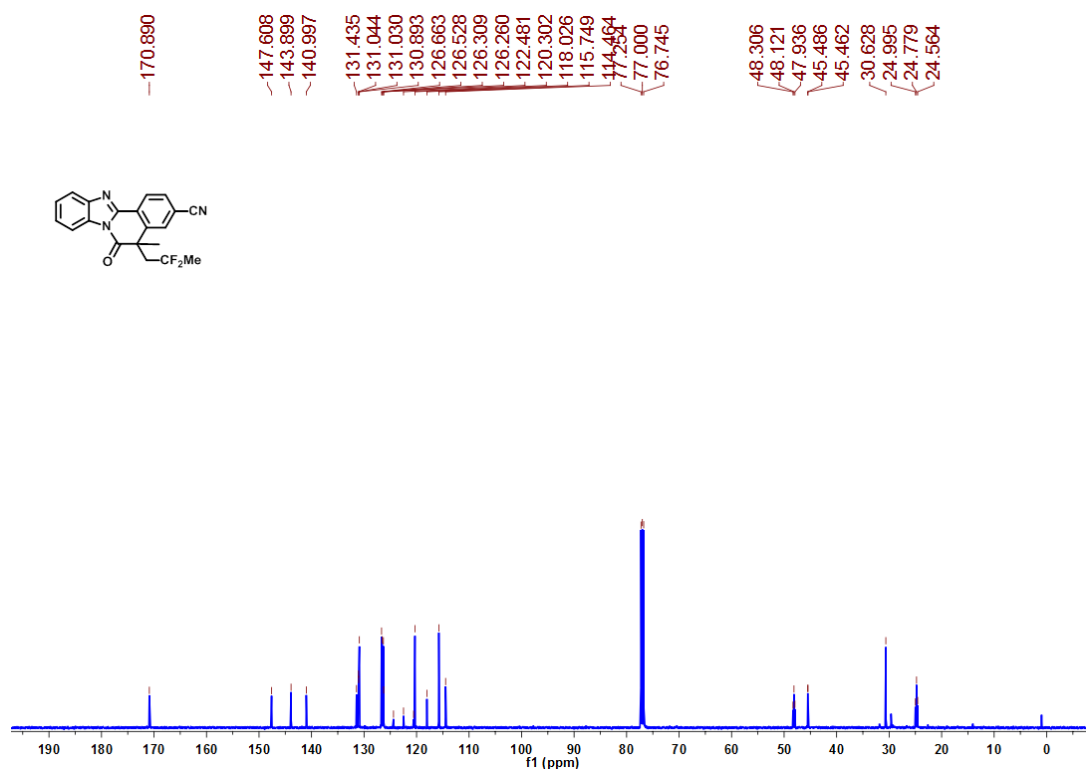
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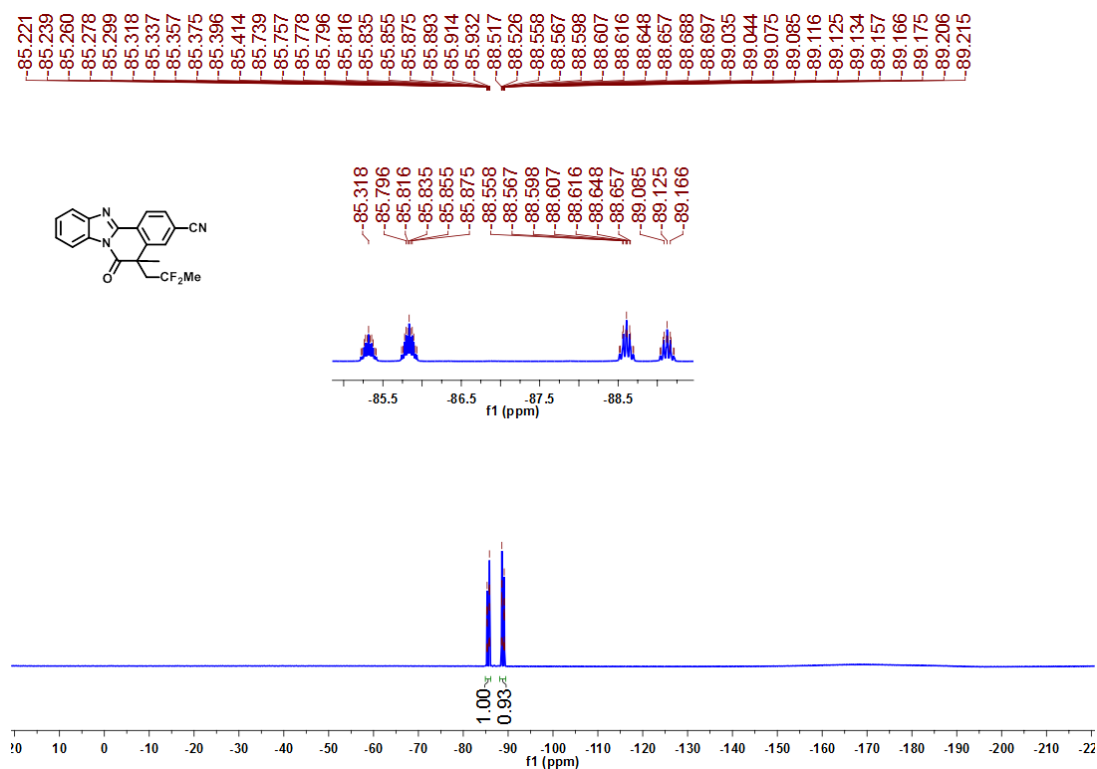
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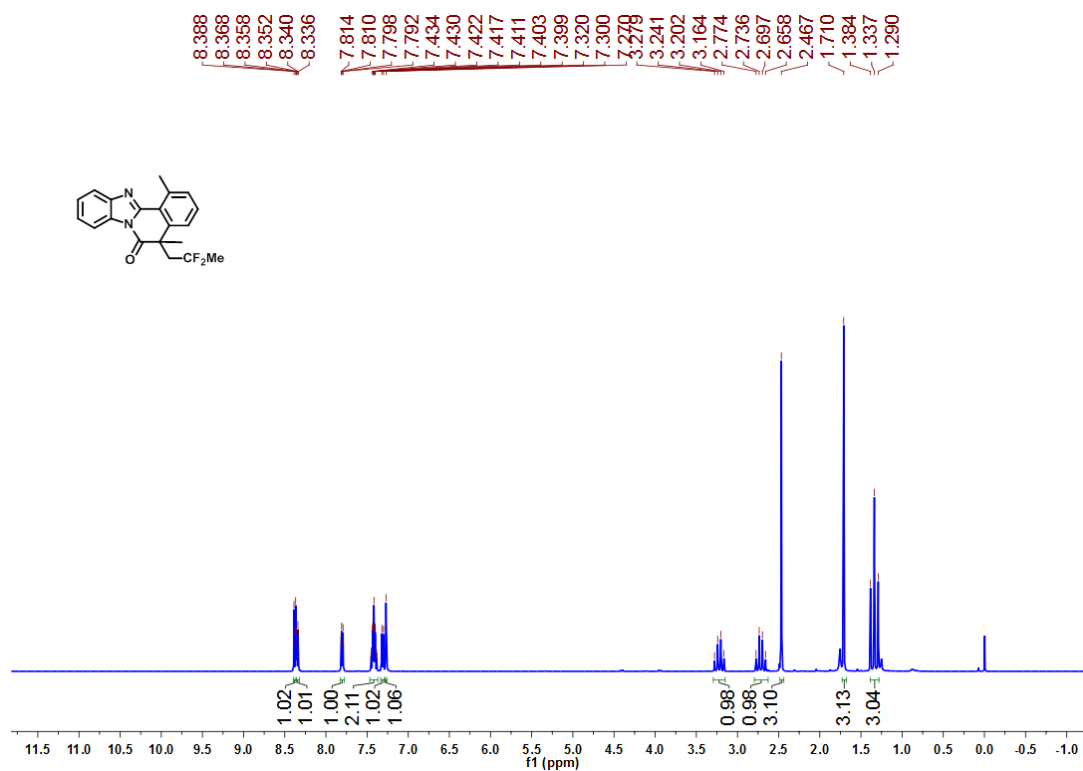
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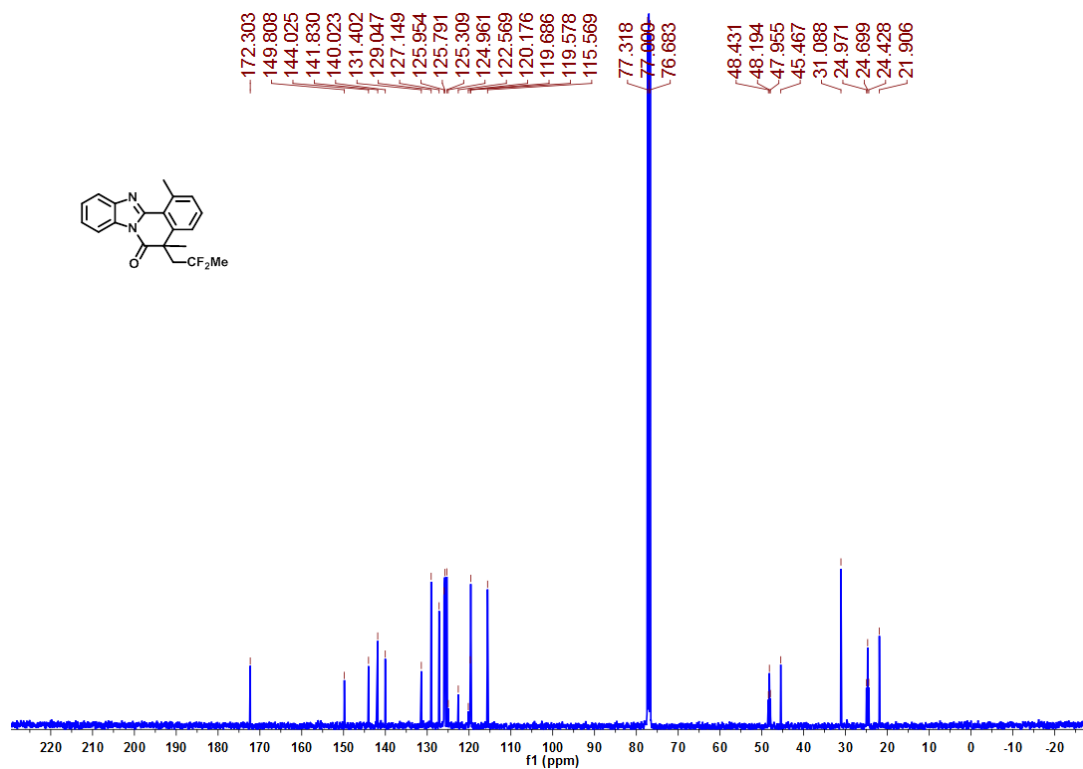
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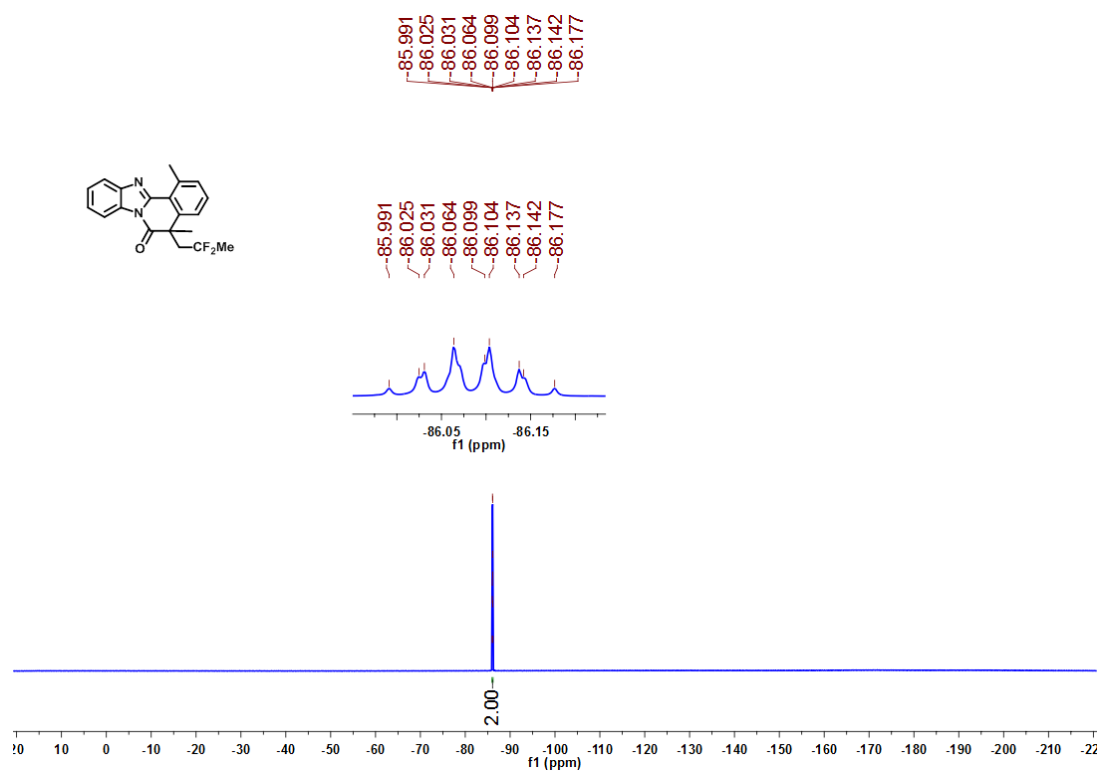
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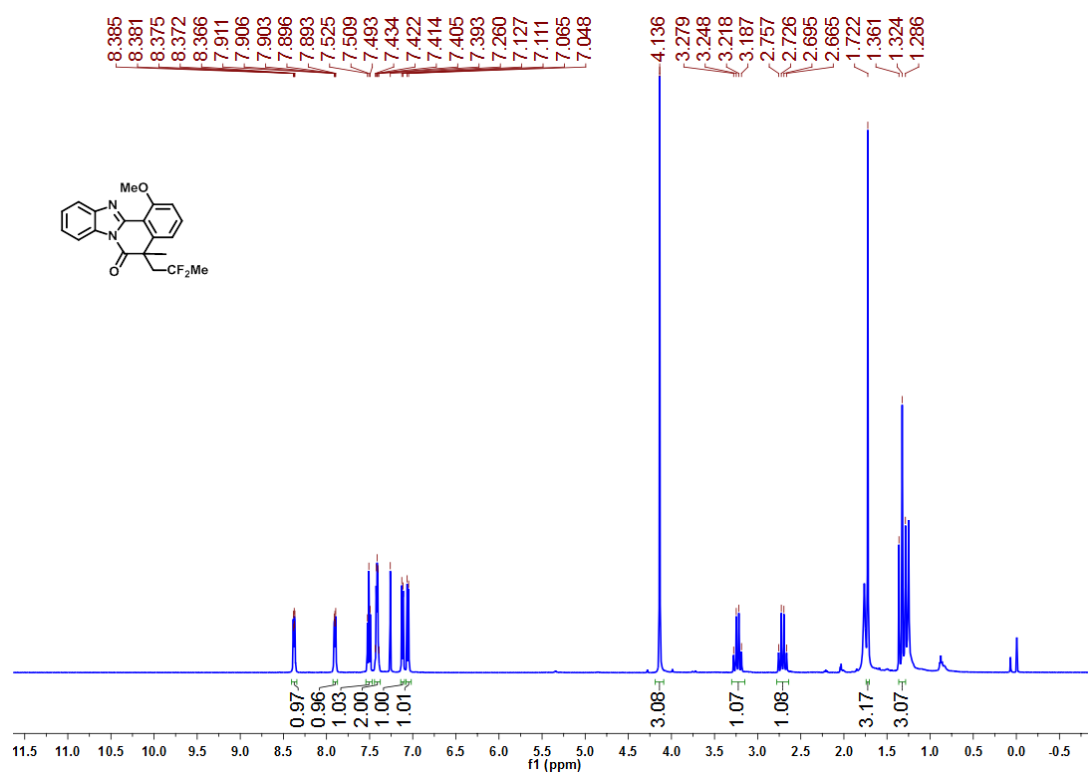
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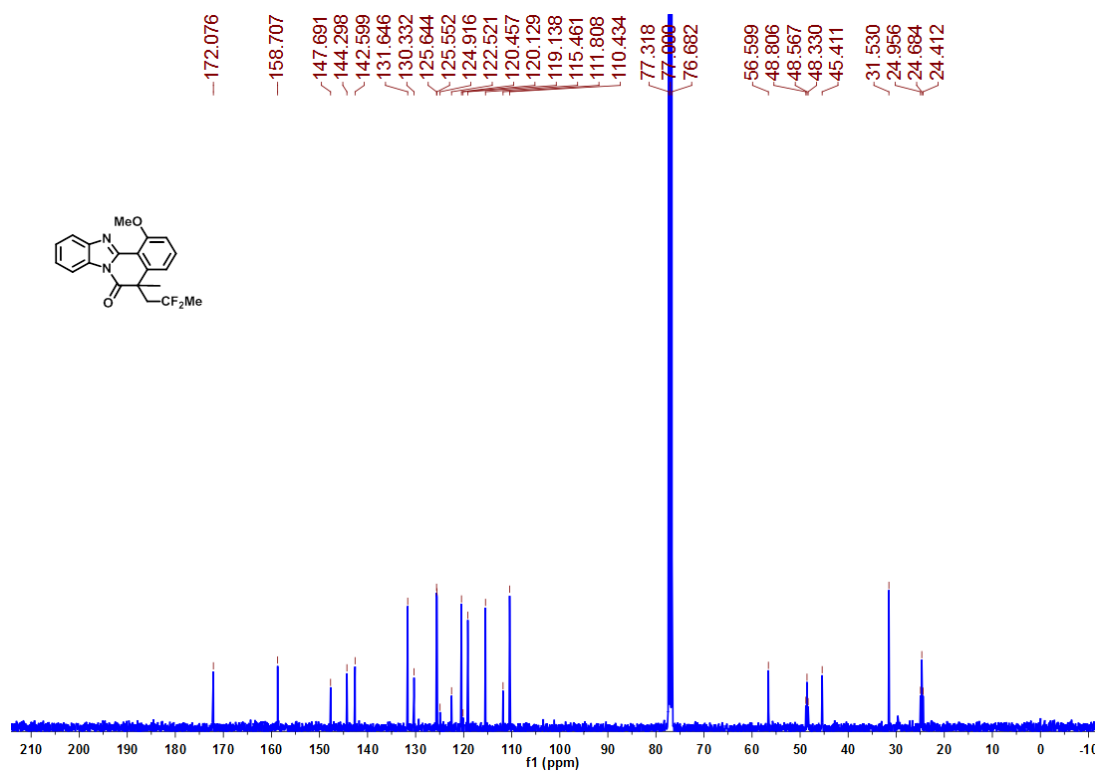
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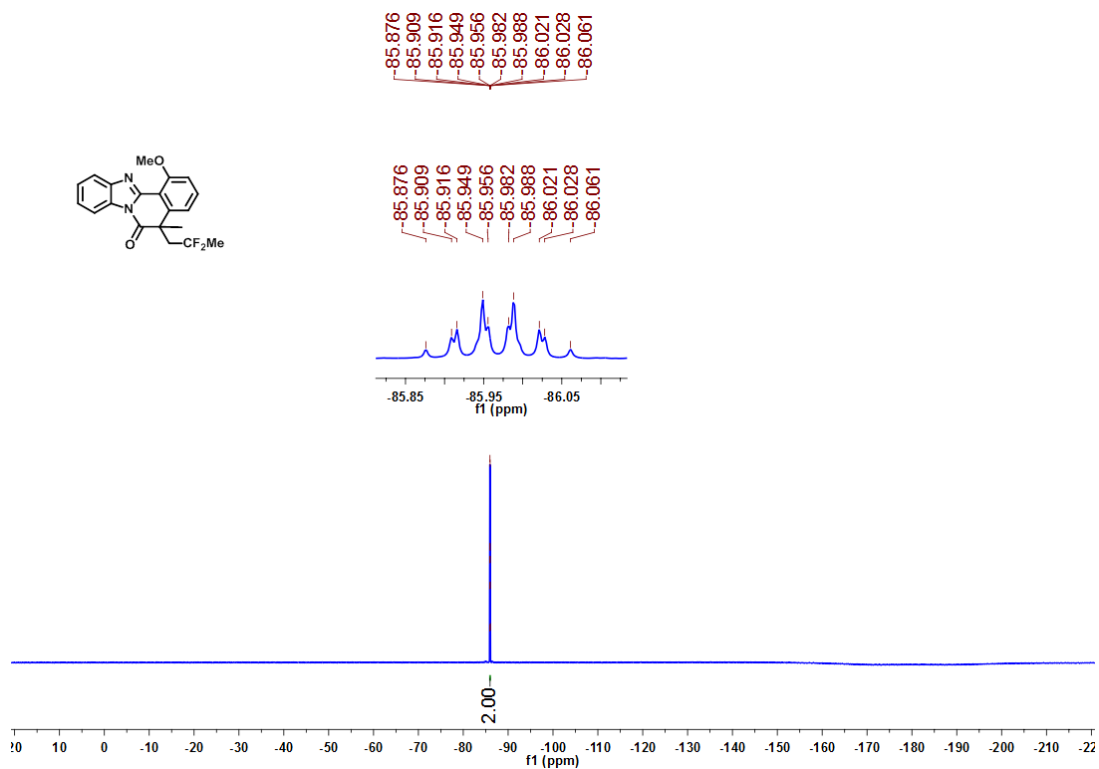
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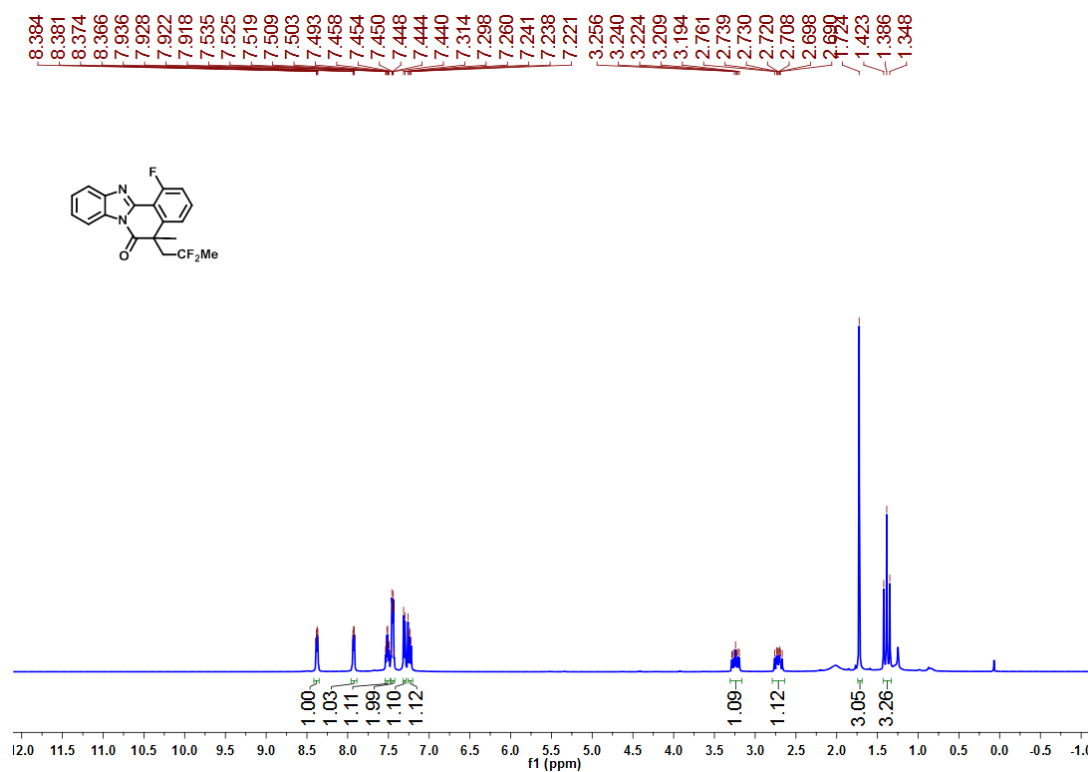
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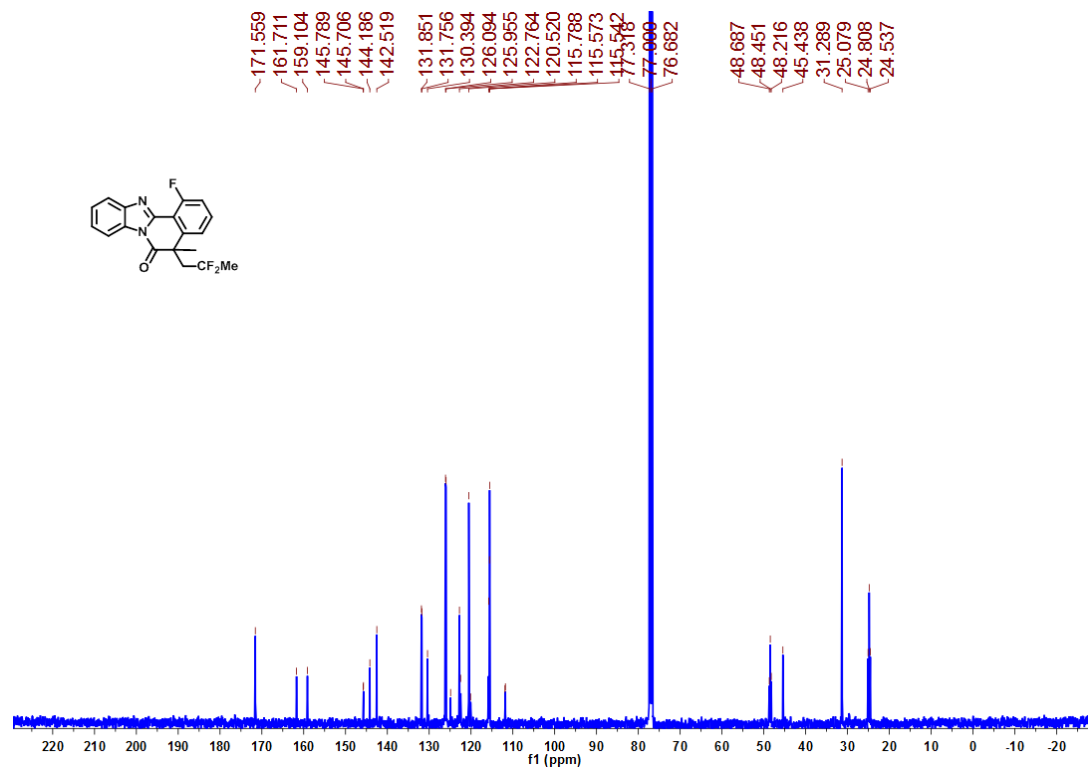
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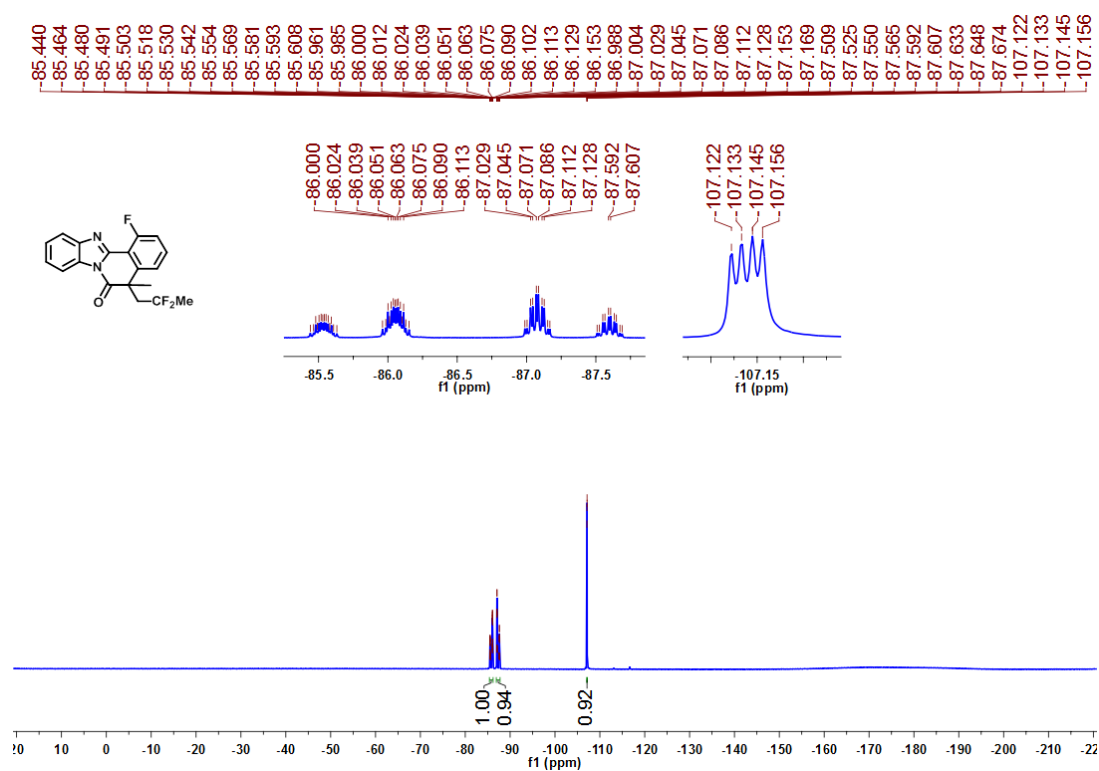
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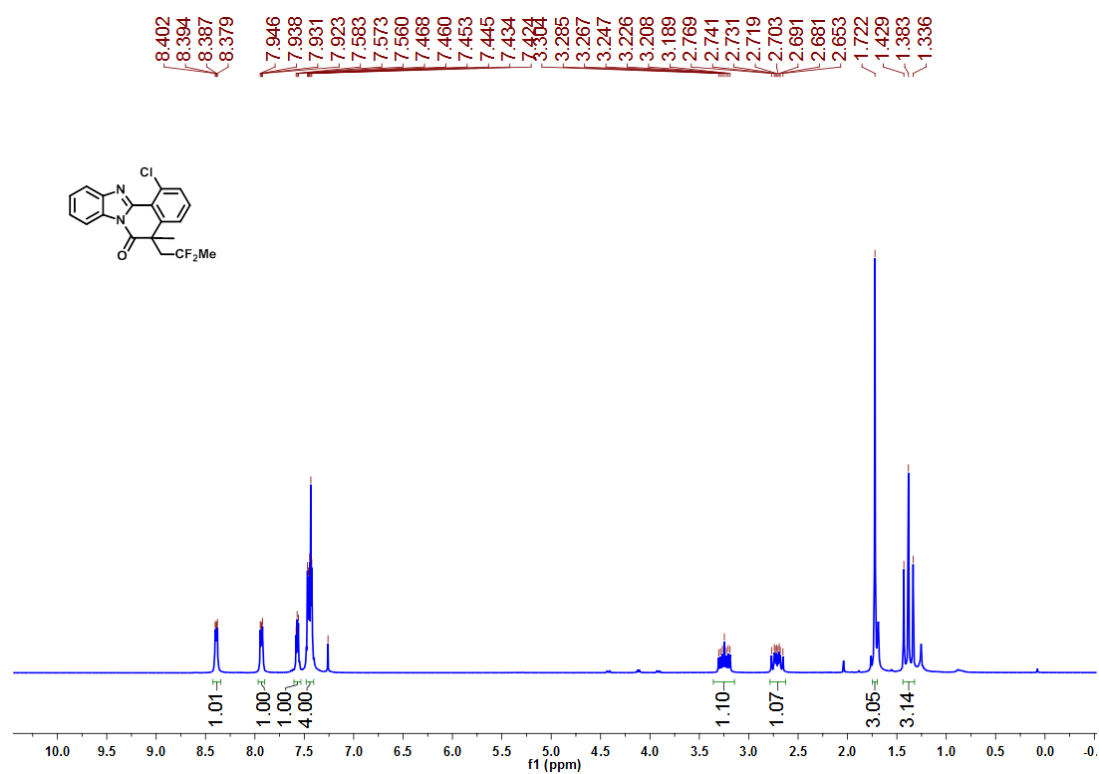
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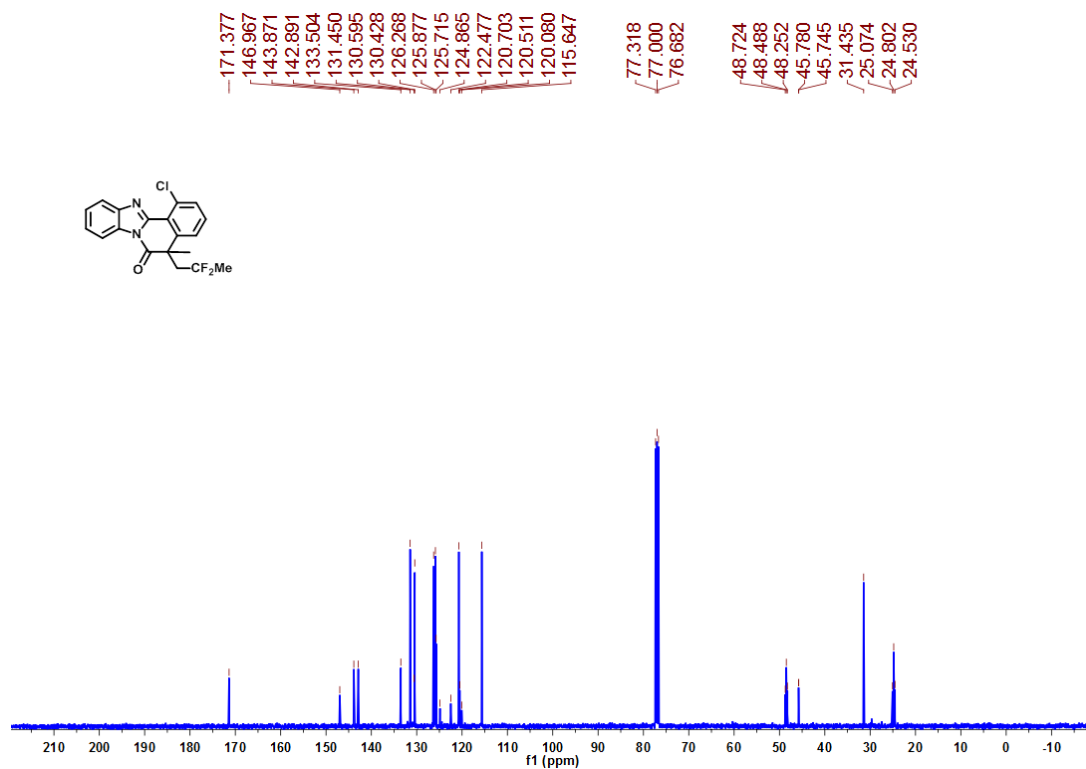
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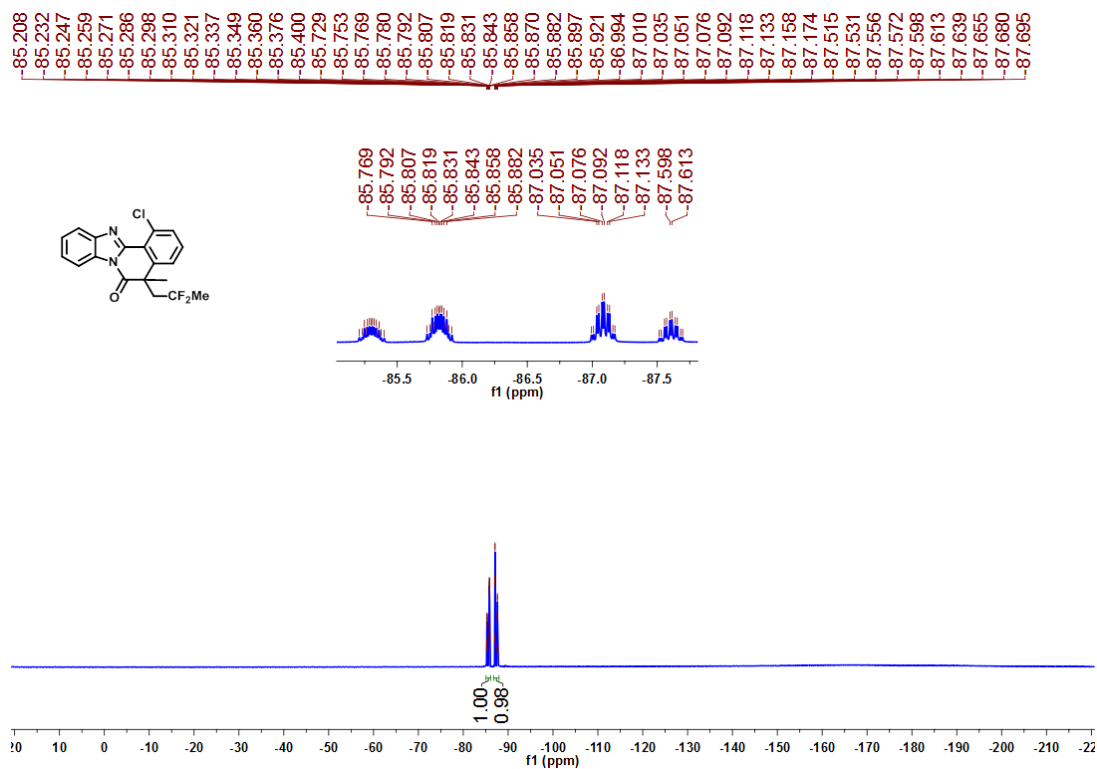
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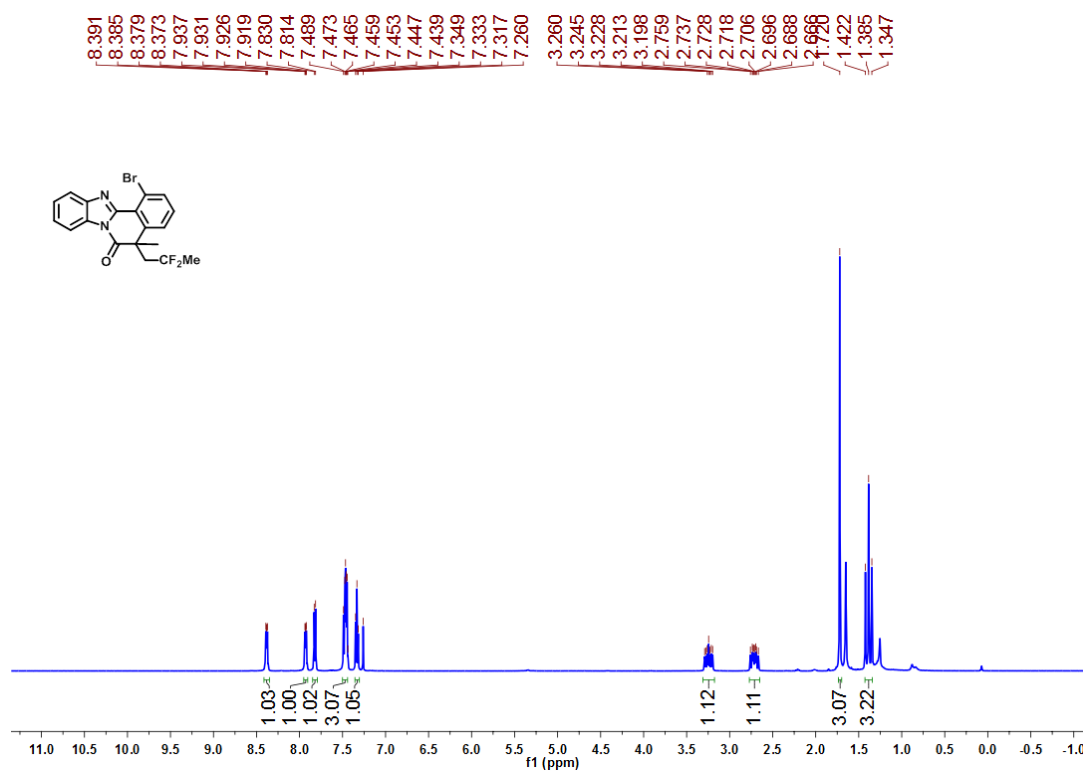
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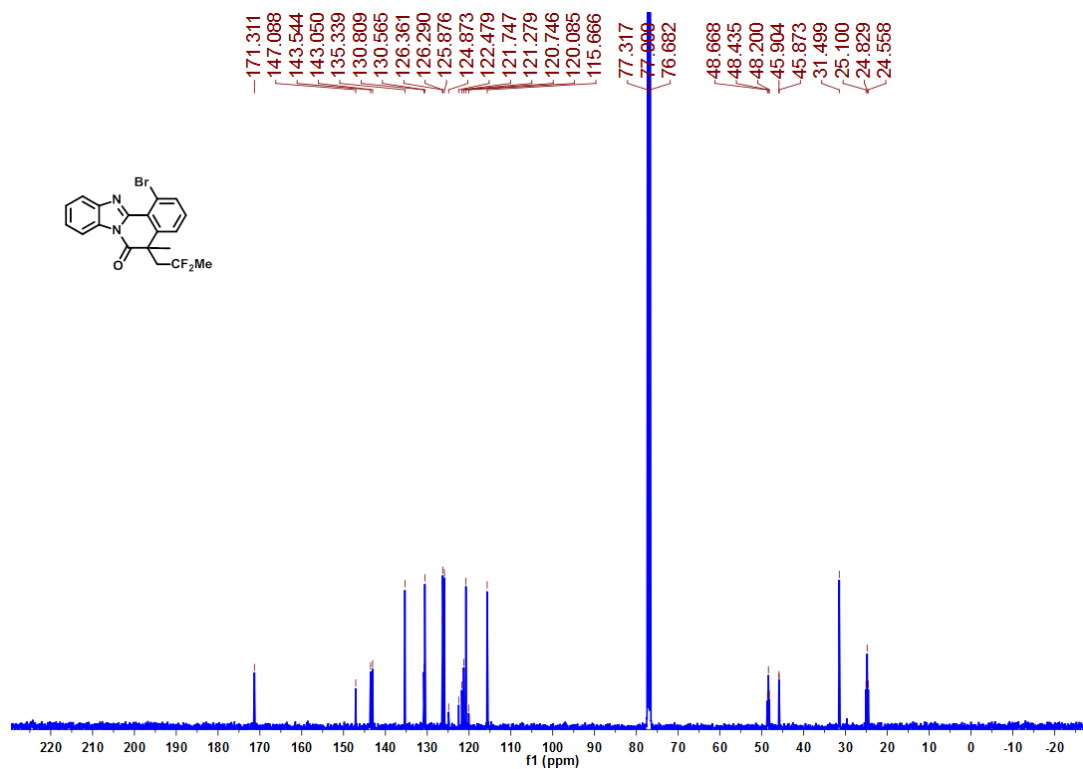
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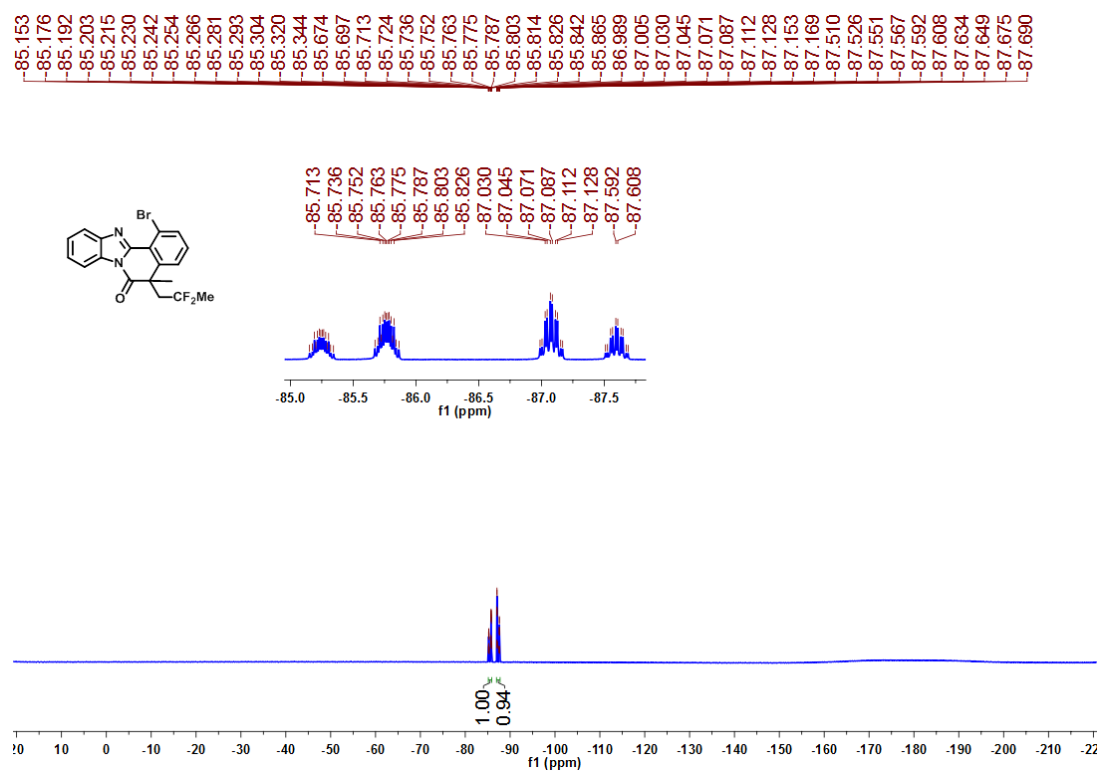
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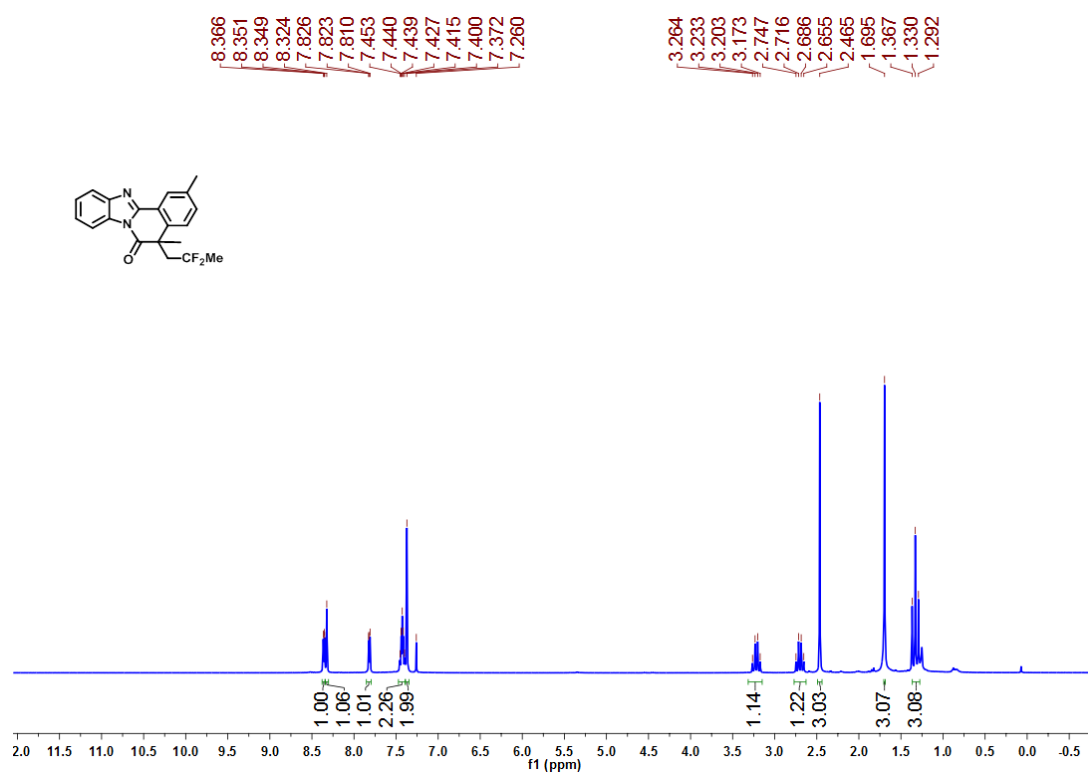
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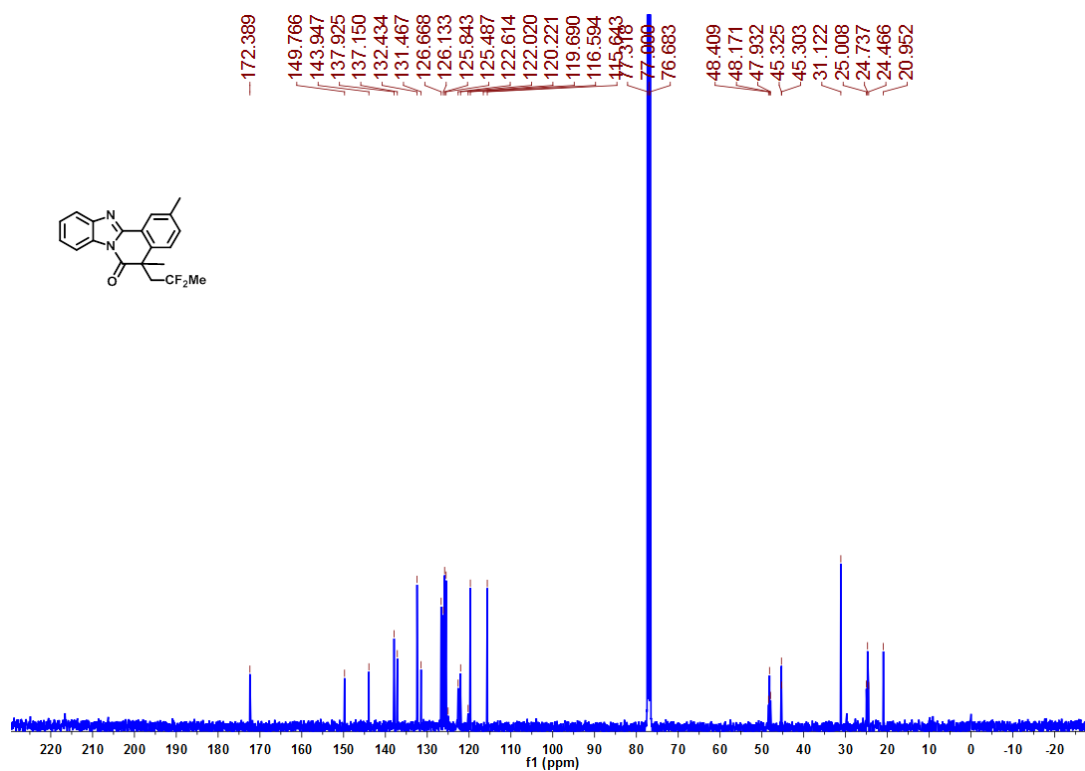
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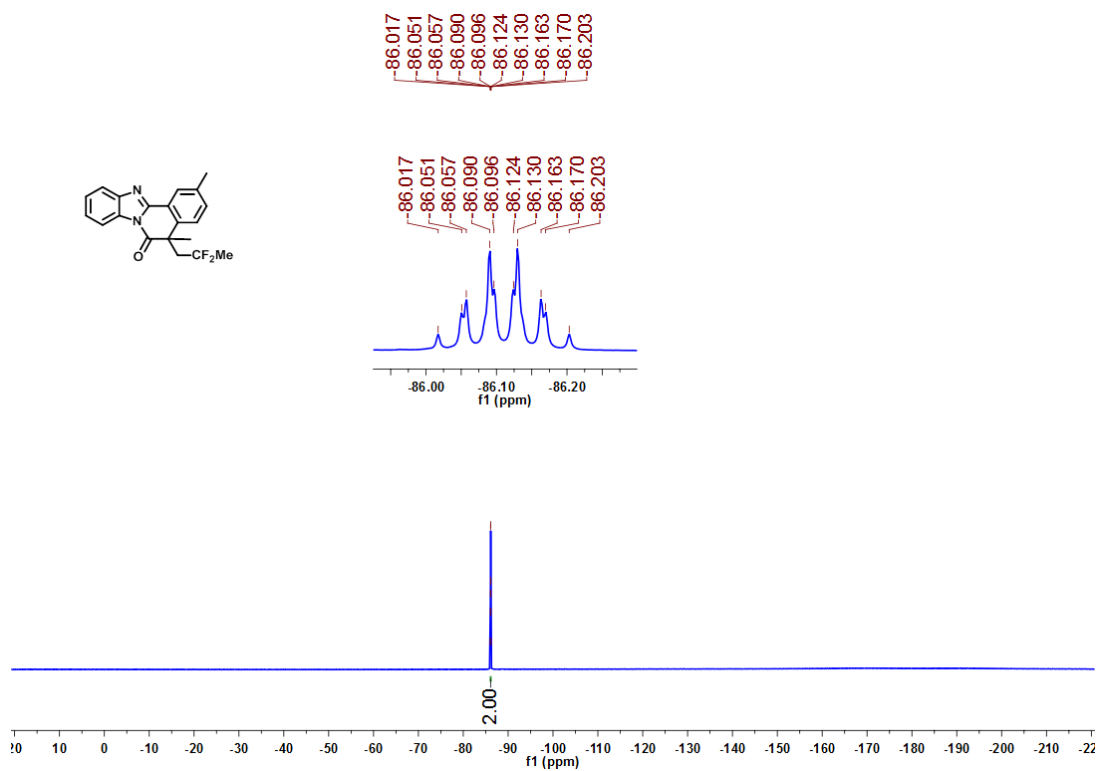
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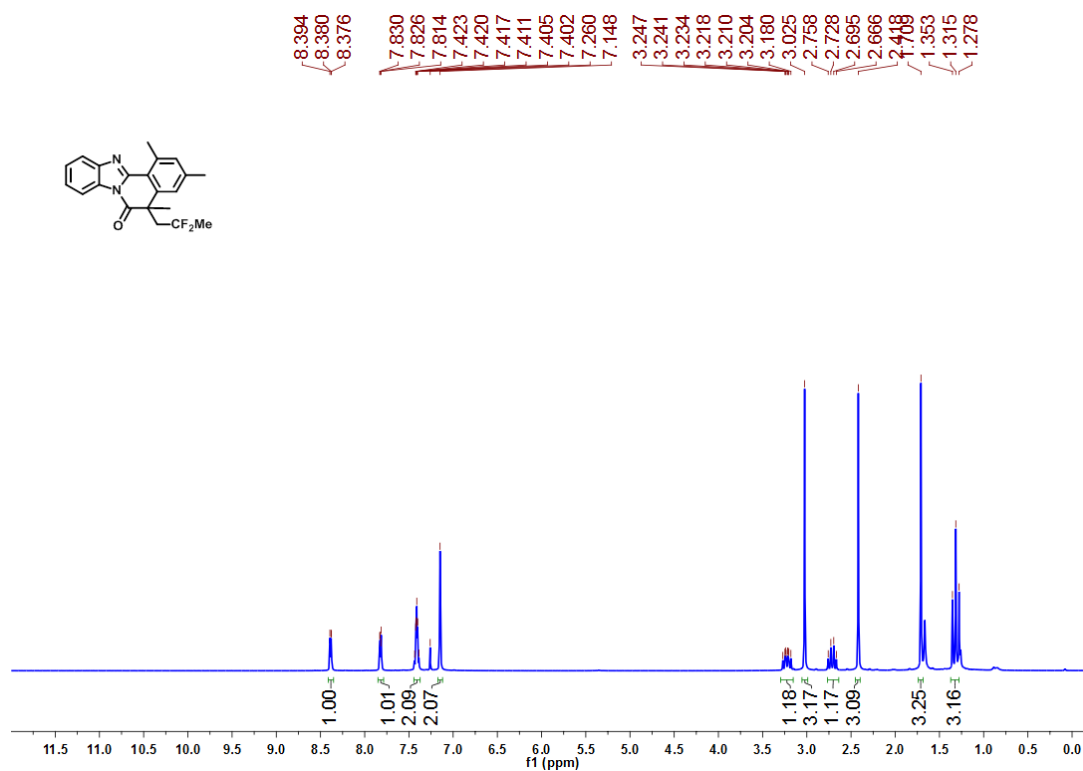
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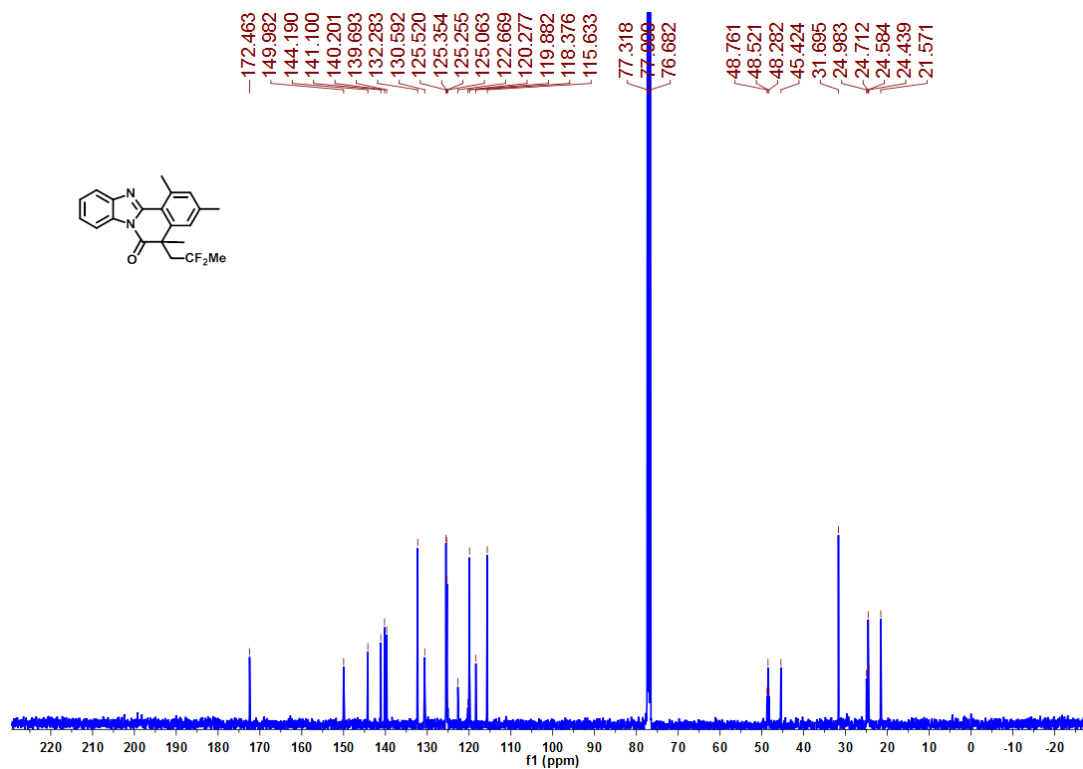
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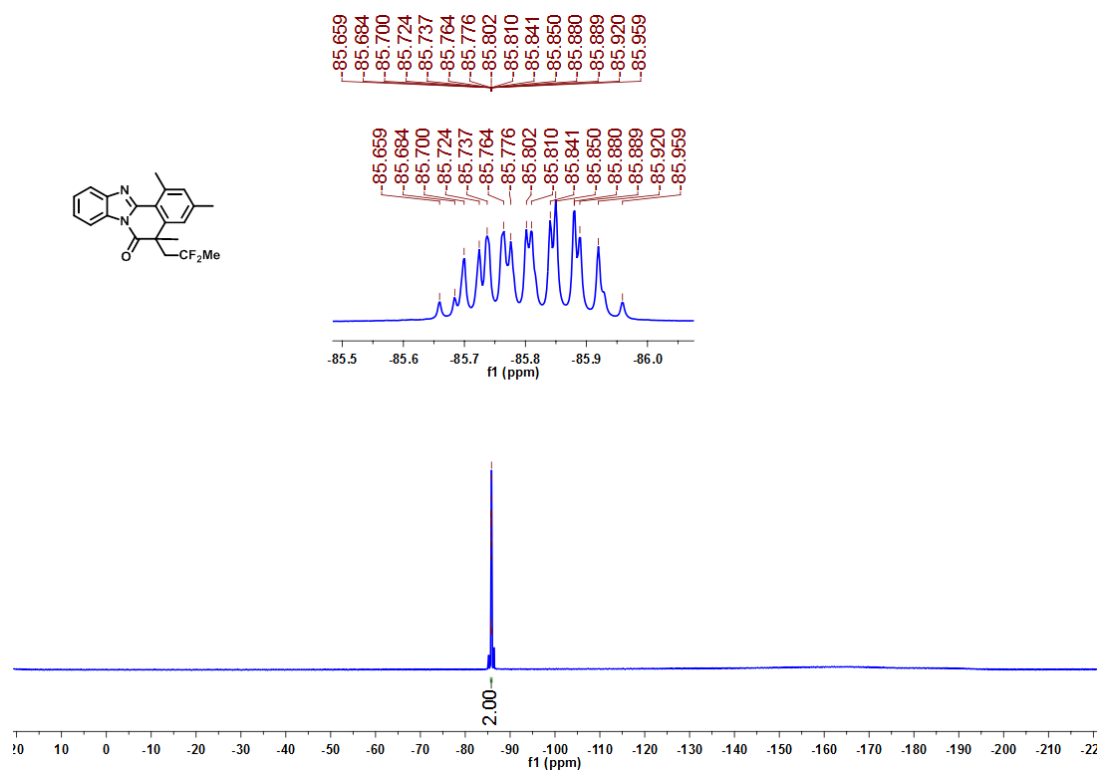
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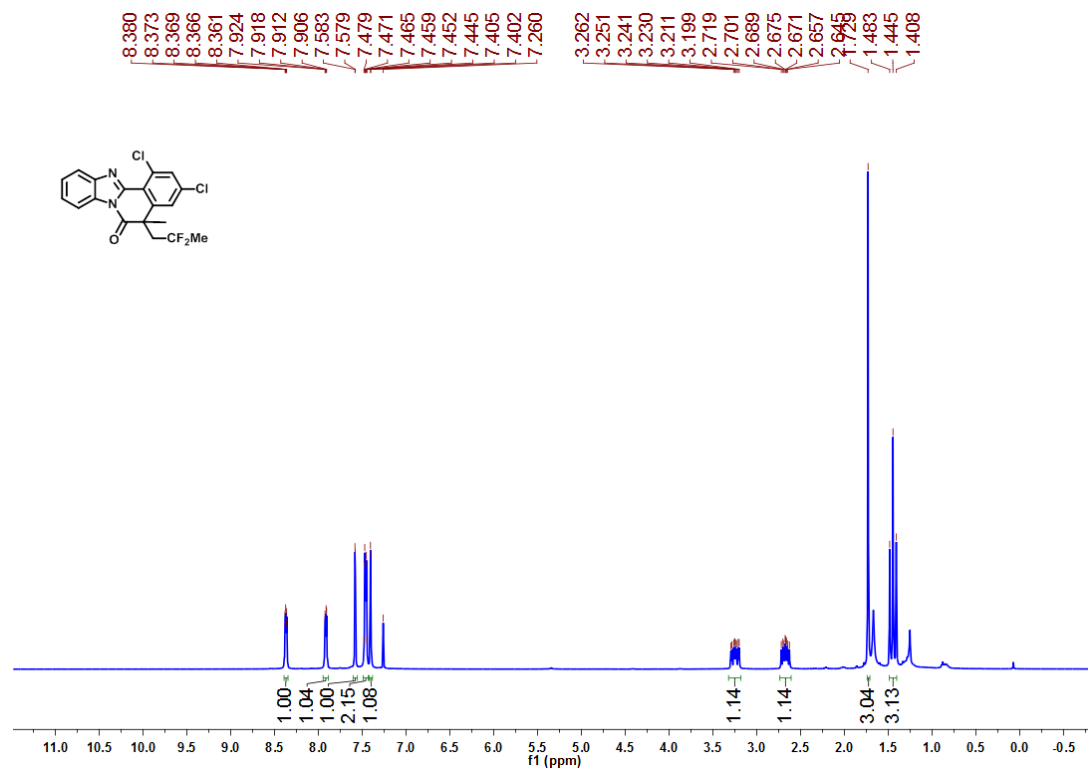
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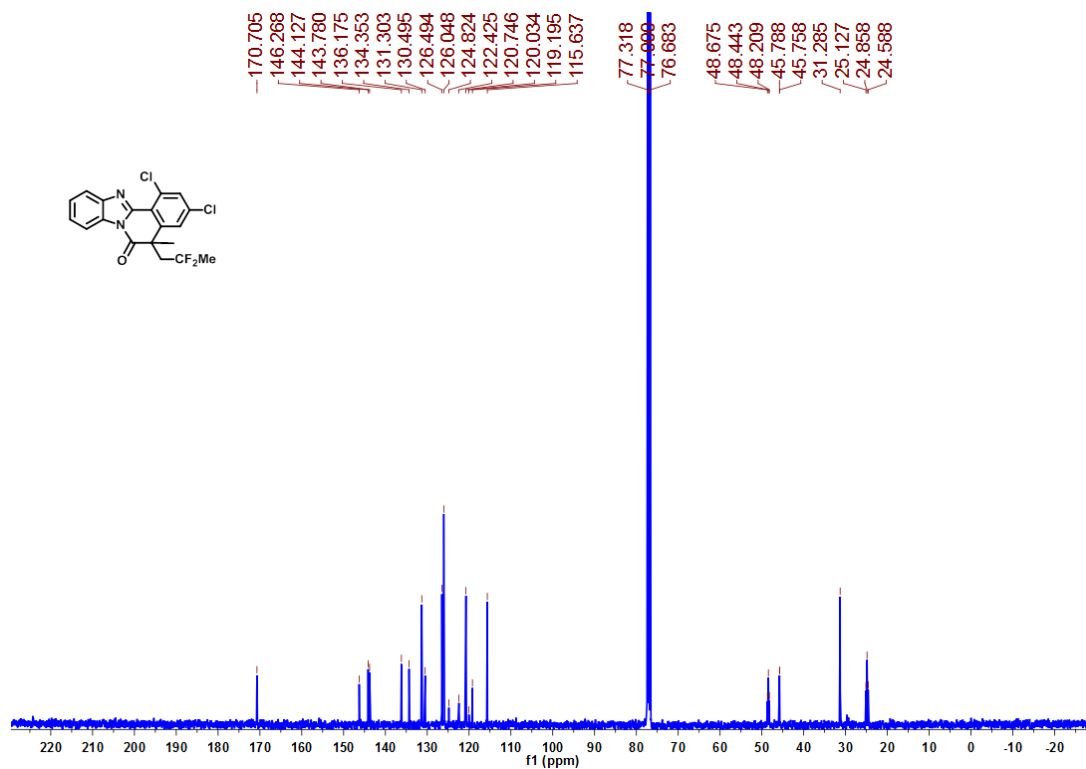
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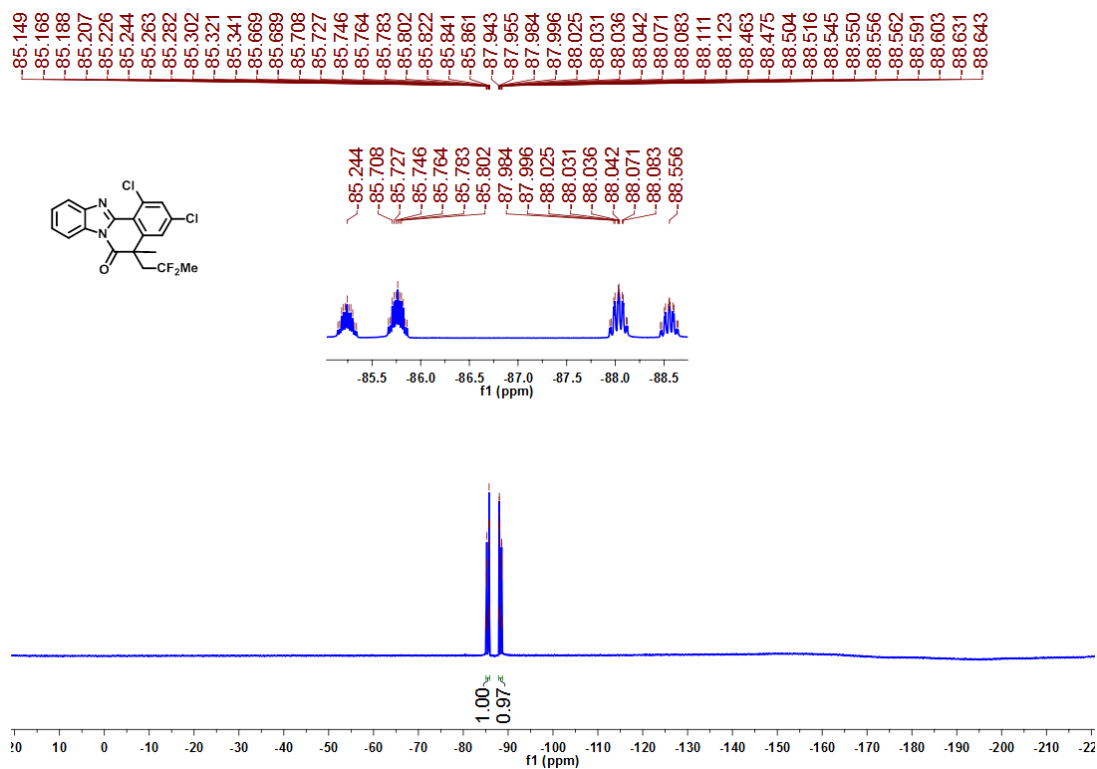
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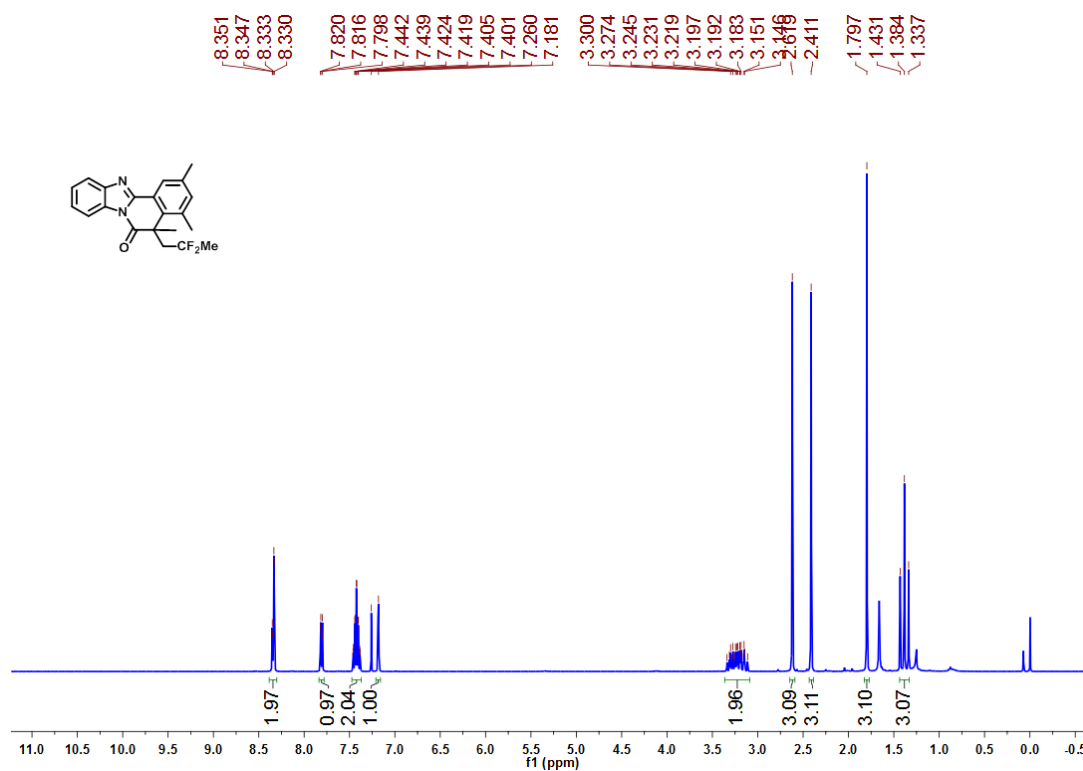
3p- $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3)



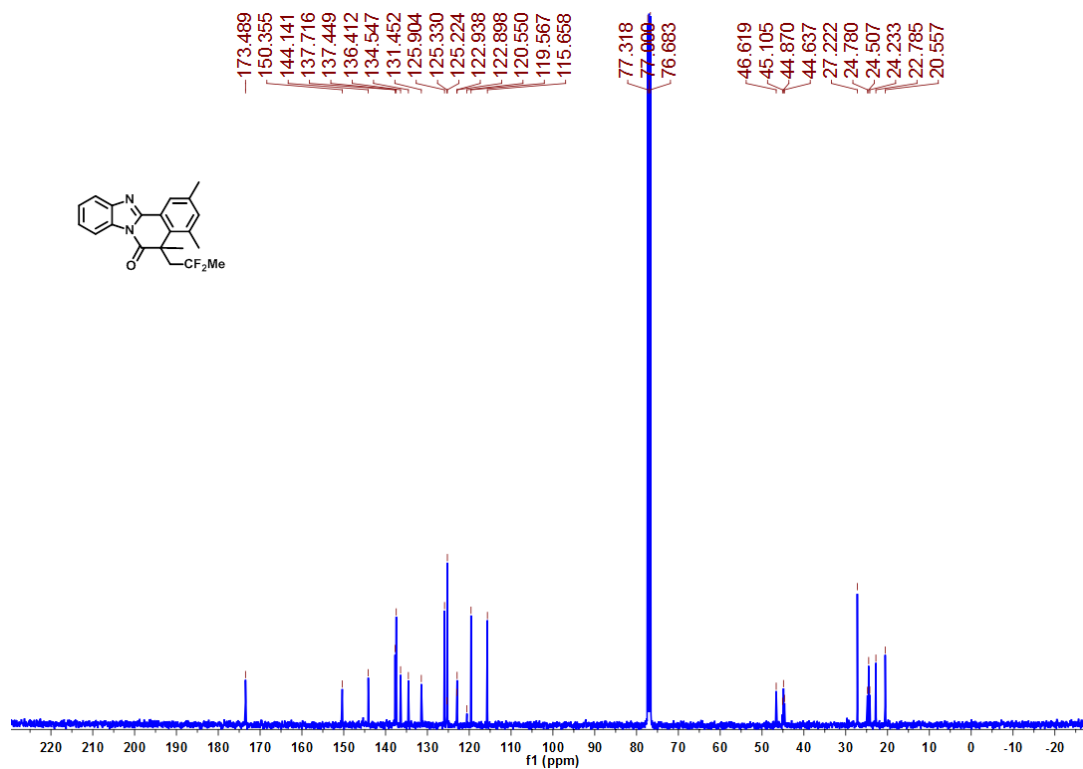
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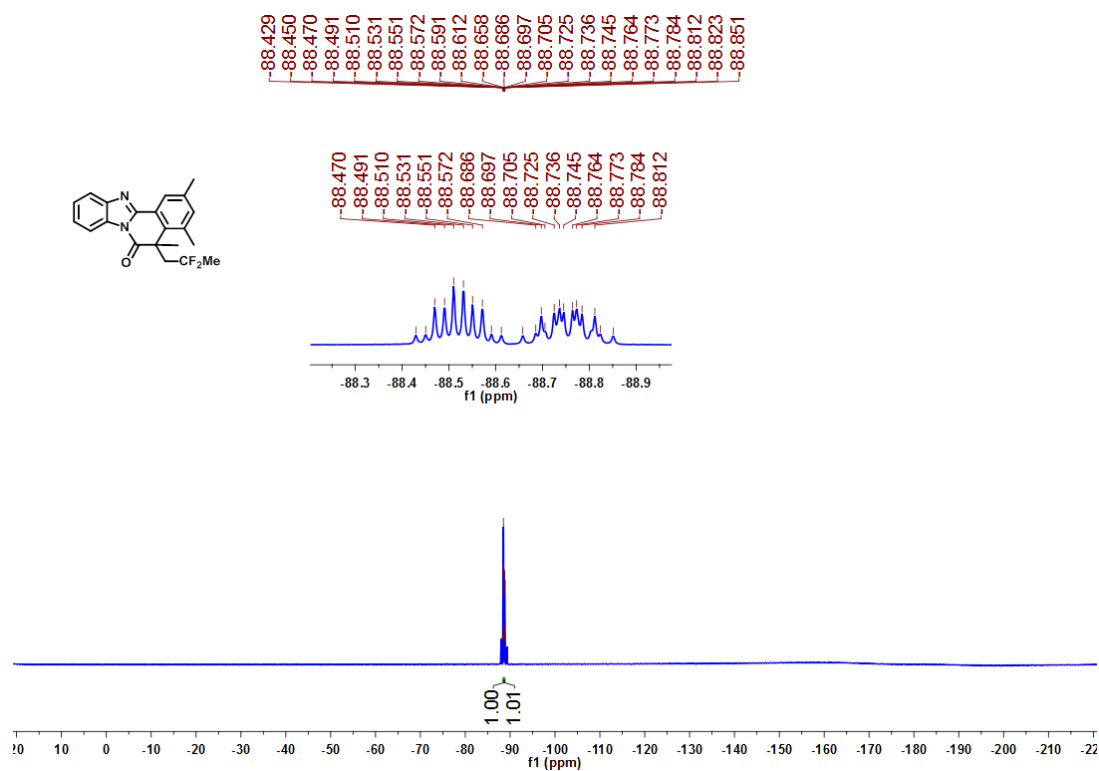
3q-¹H NMR (400 MHz, CDCl₃)



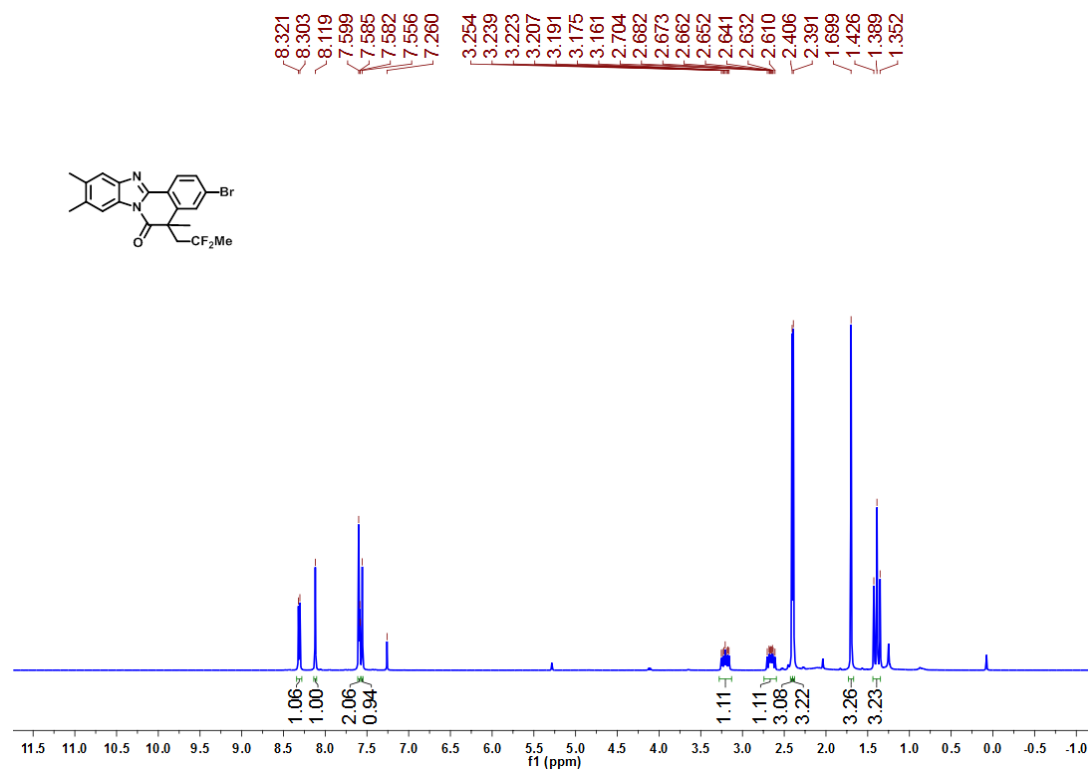
3q-¹³C{¹H} NMR (100 MHz, CDCl₃)



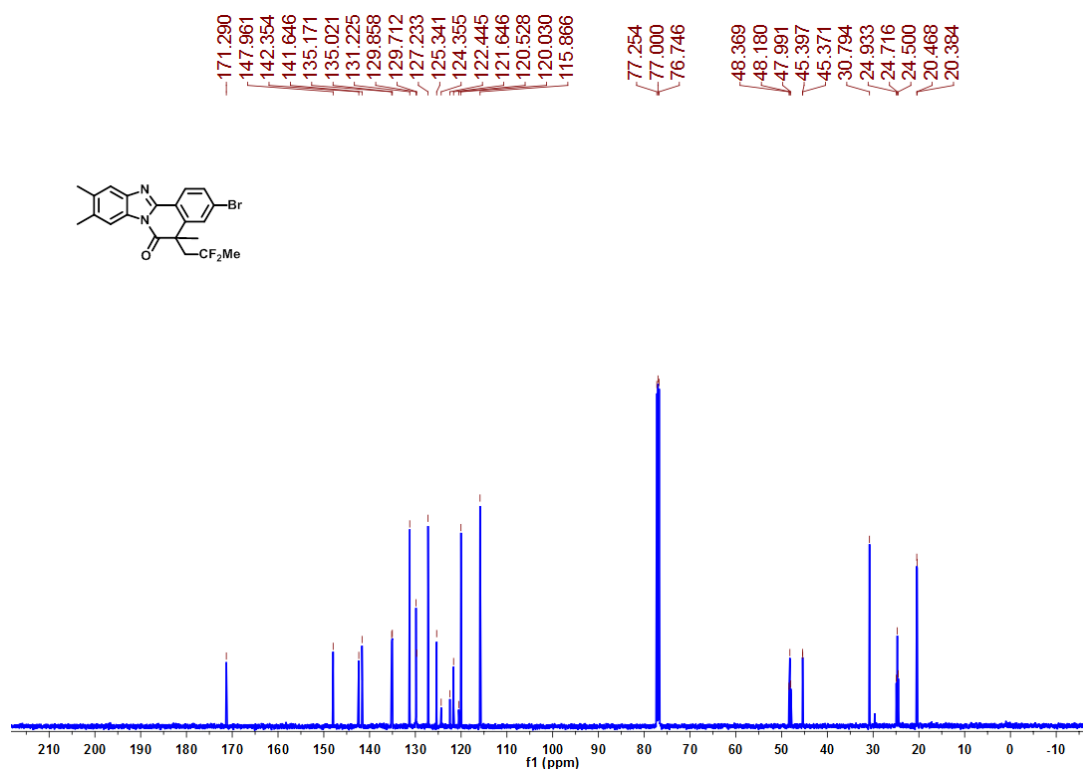
3q-¹⁹F NMR (471 MHz, CDCl₃)



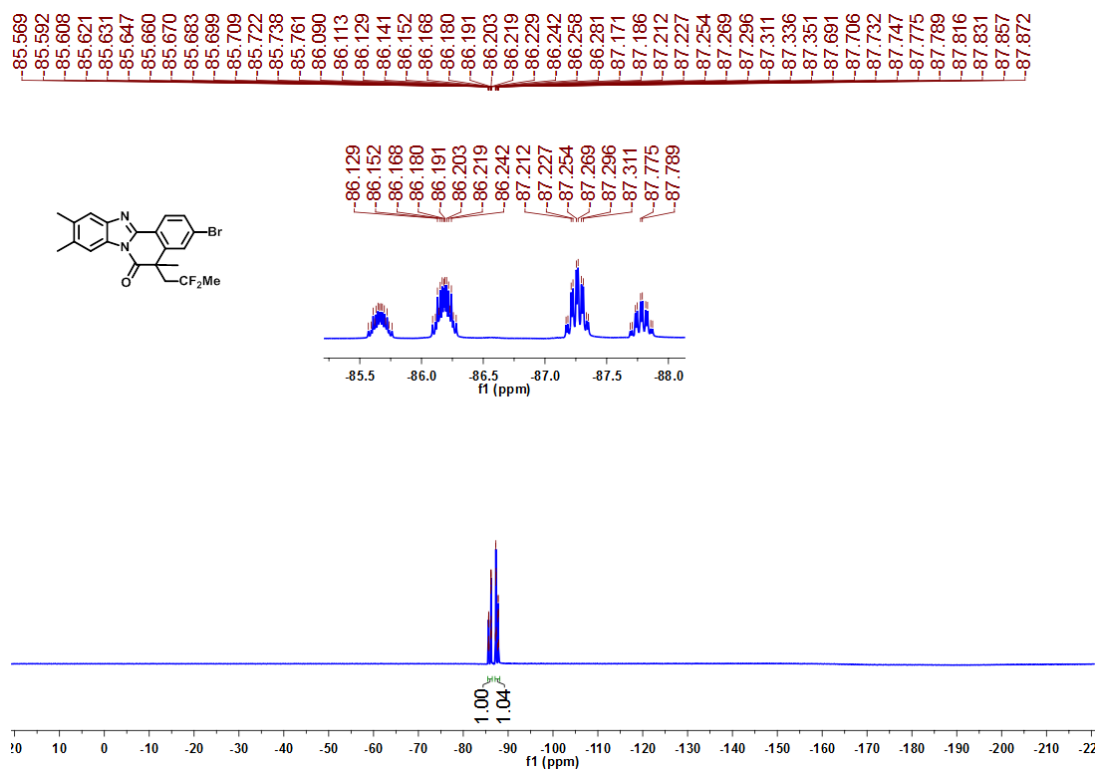
3r-¹H NMR (500 MHz, CDCl₃)



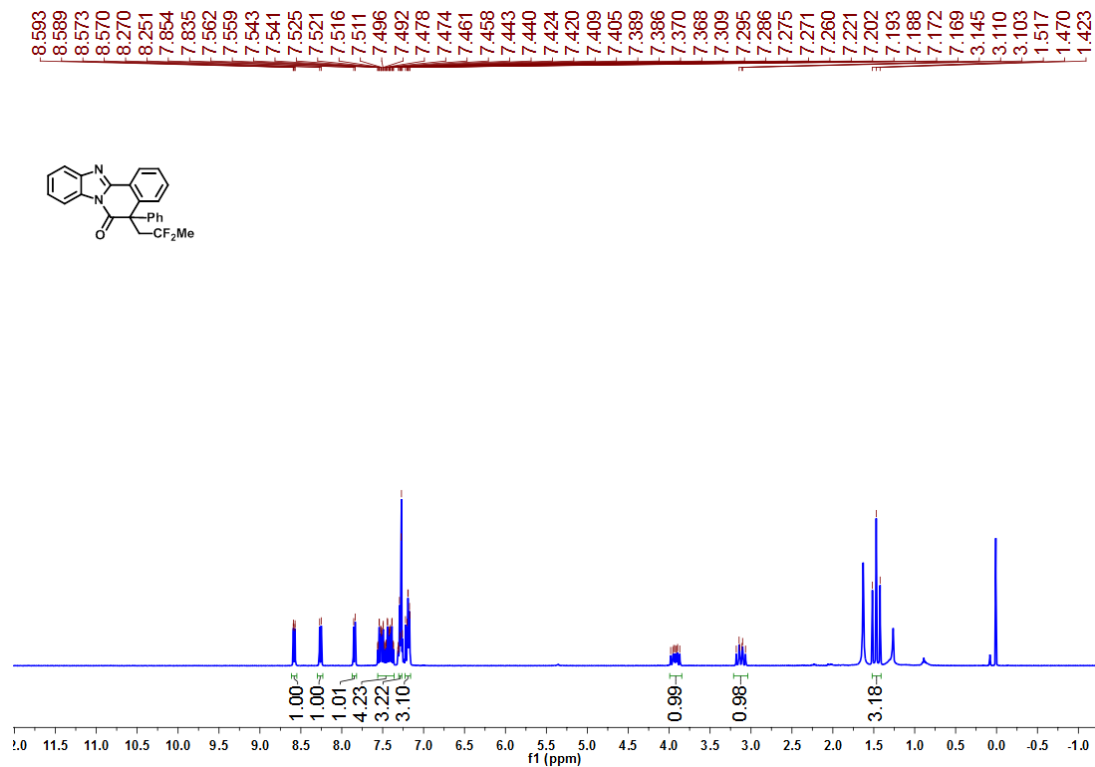
3r-¹³C{¹H} NMR (125 MHz, CDCl₃)



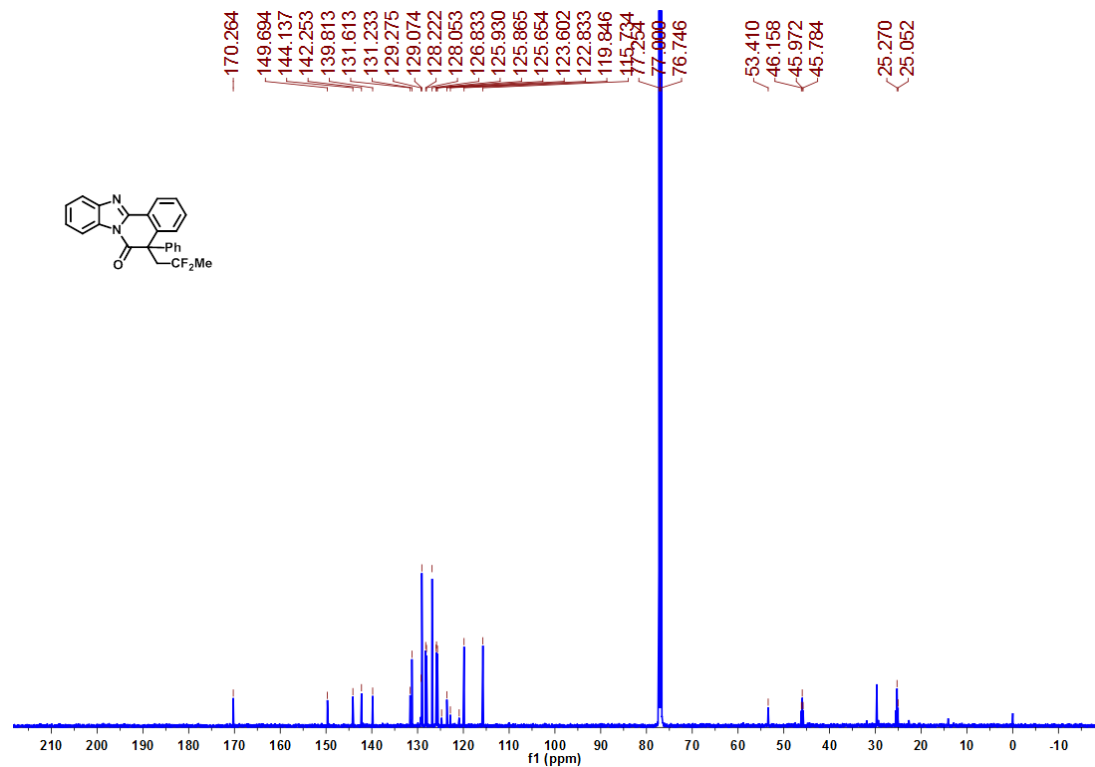
3r-¹⁹F NMR (471 MHz, CDCl₃)



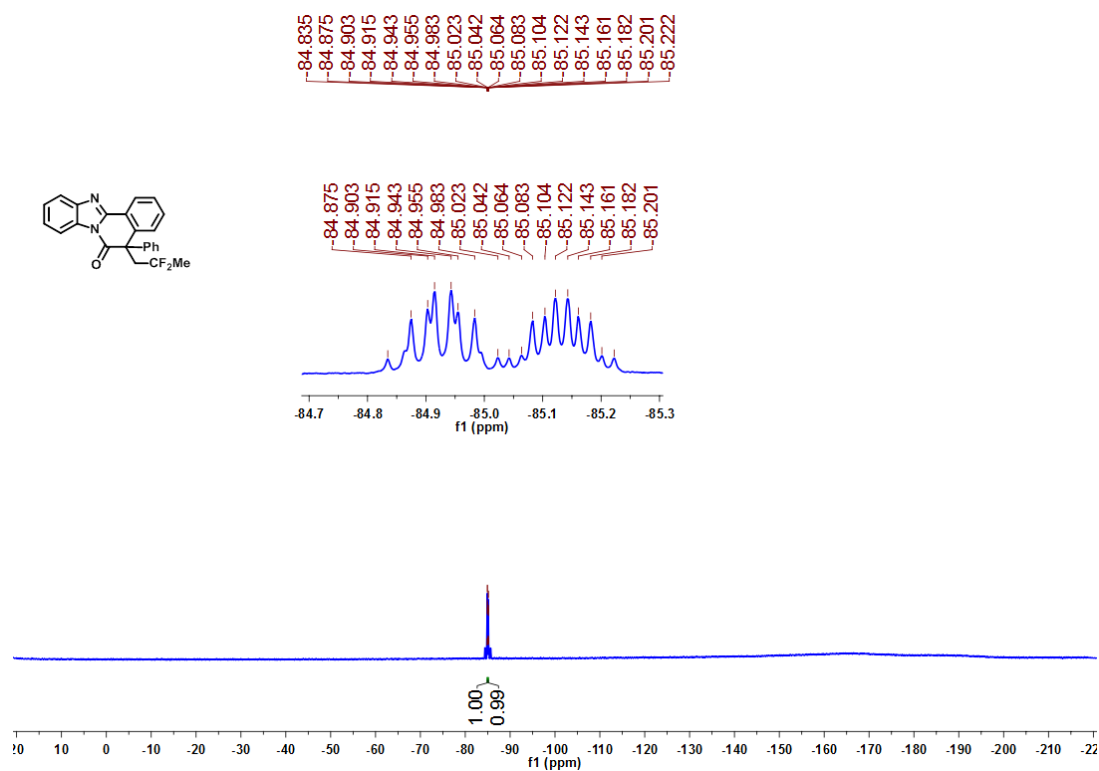
3s-¹H NMR (400 MHz, CDCl₃)



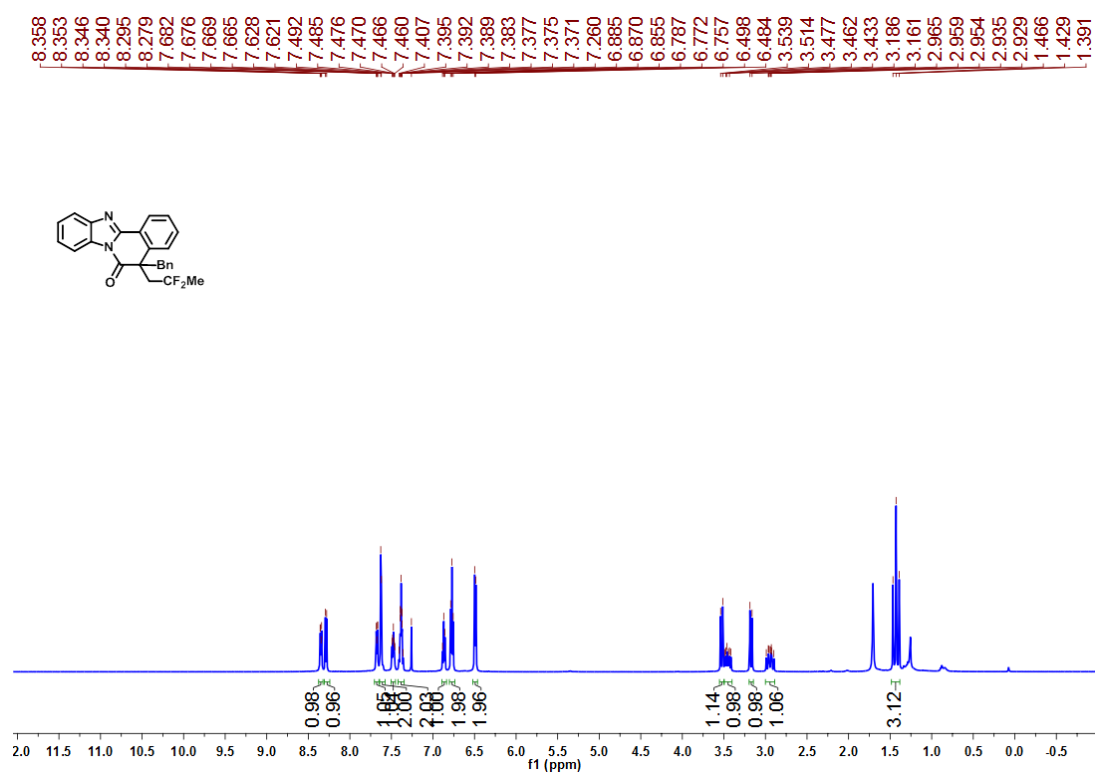
3s-¹³C{¹H} NMR (125 MHz, CDCl₃)



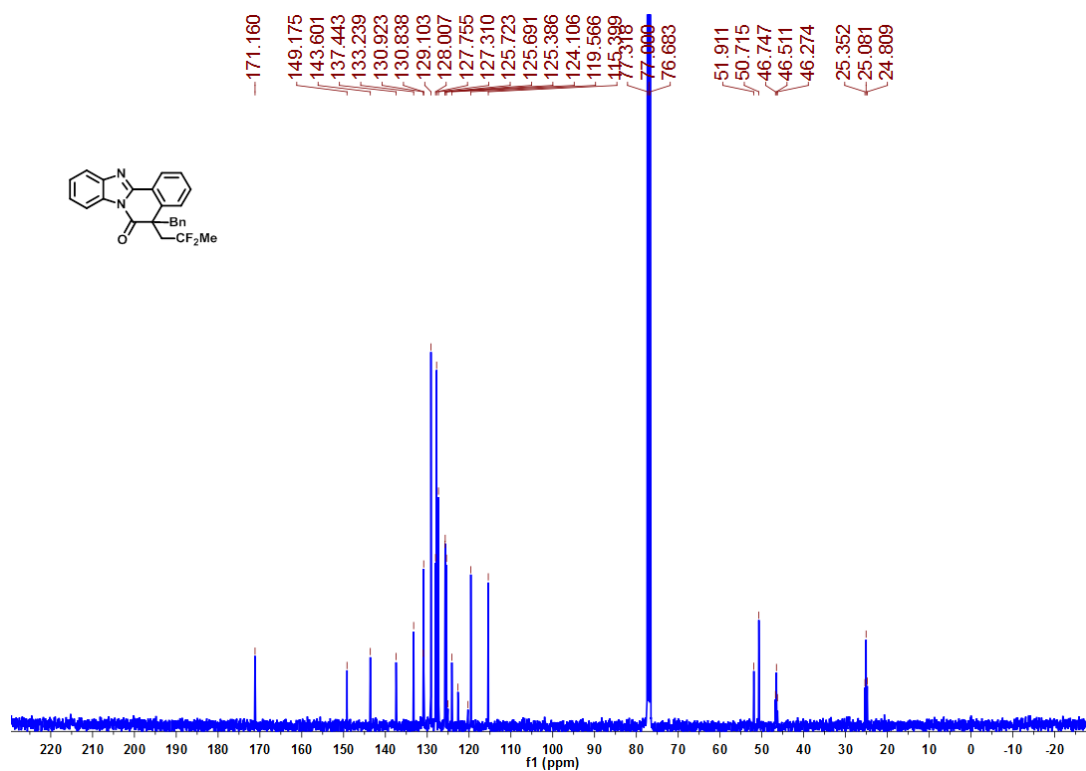
3s-¹⁹F NMR (471 MHz, CDCl₃)



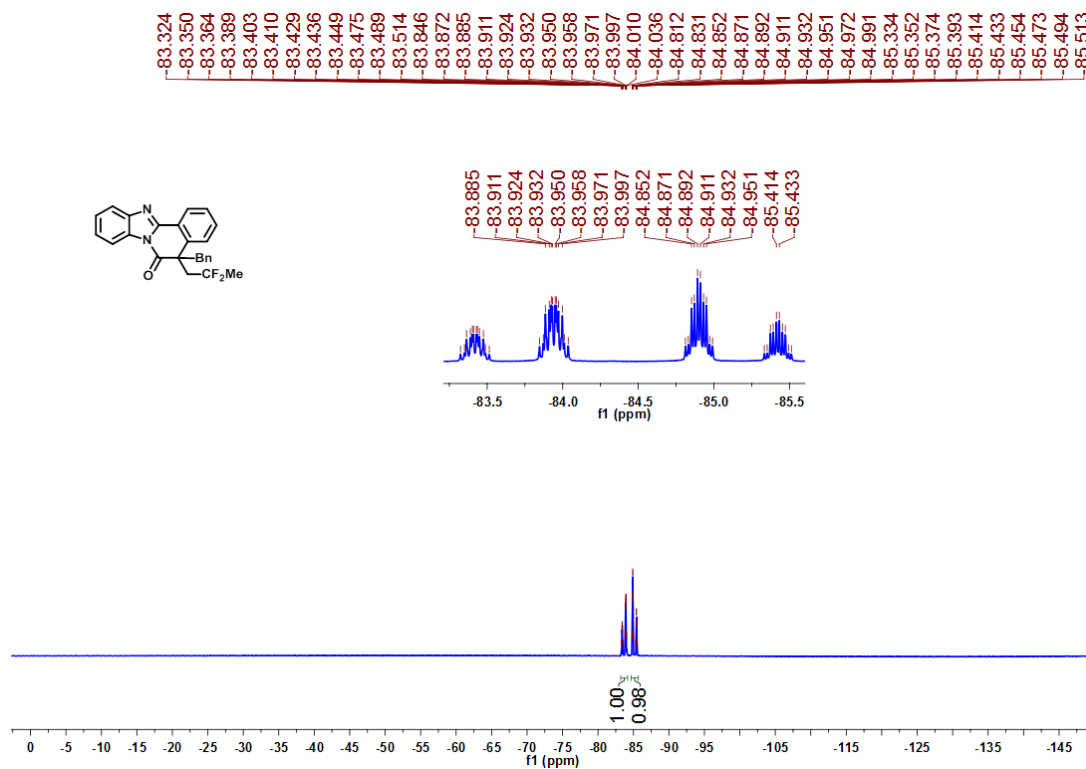
3t-¹H NMR (500 MHz, CDCl₃)



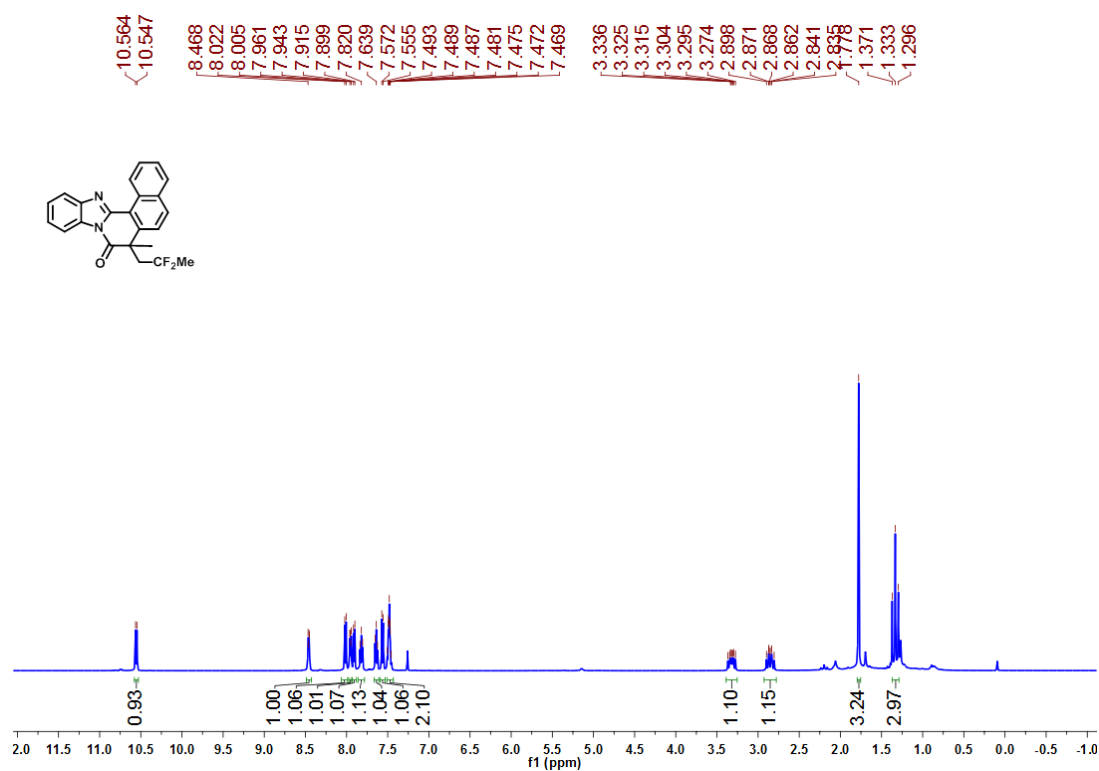
3t-¹³C{¹H} NMR (100 MHz, CDCl₃)



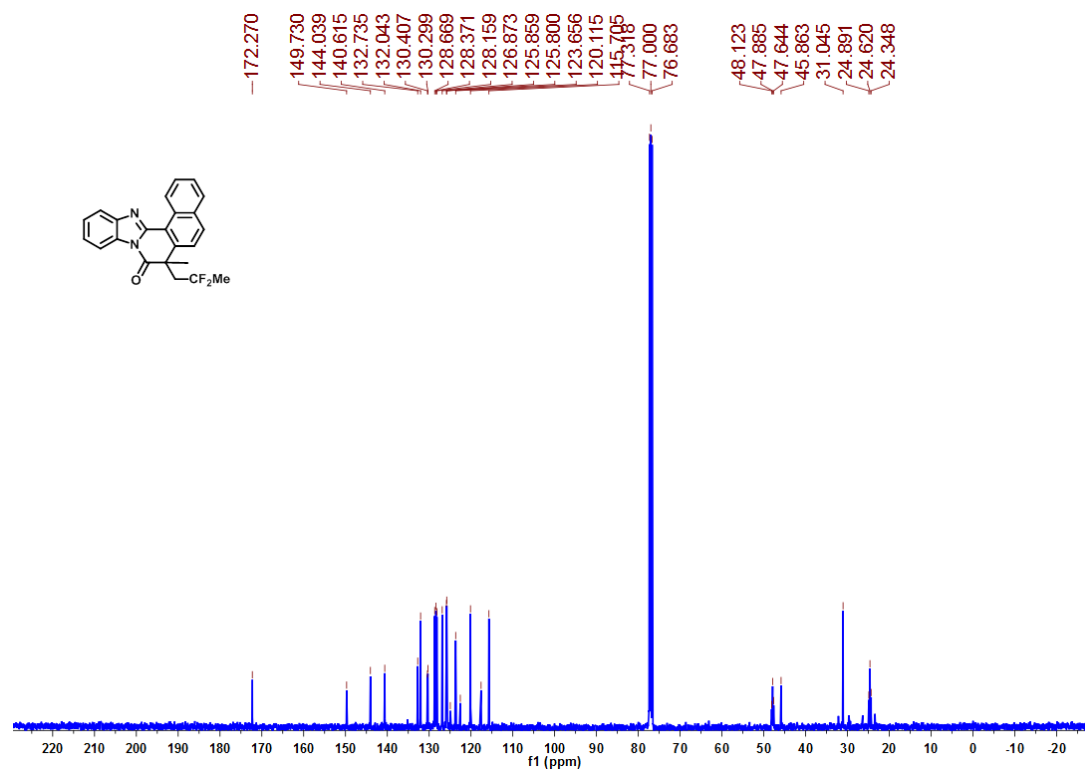
3t-¹⁹F NMR (471 MHz, CDCl₃)



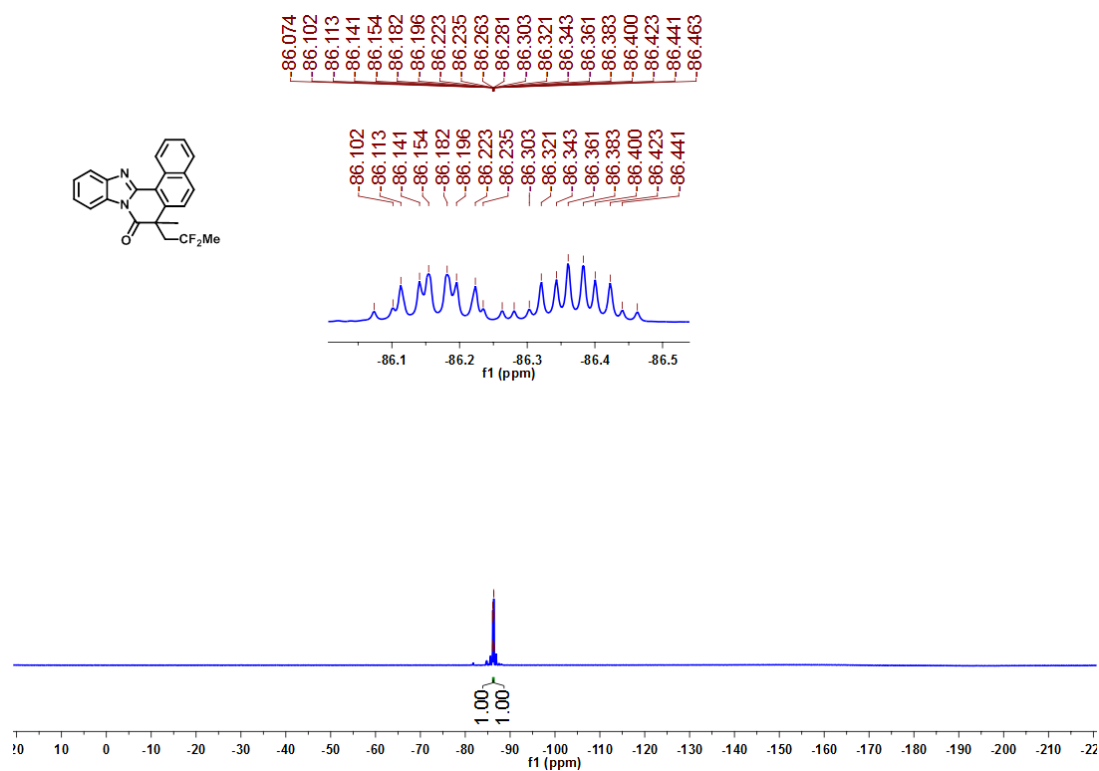
3u-¹H NMR (500 MHz, CDCl₃)



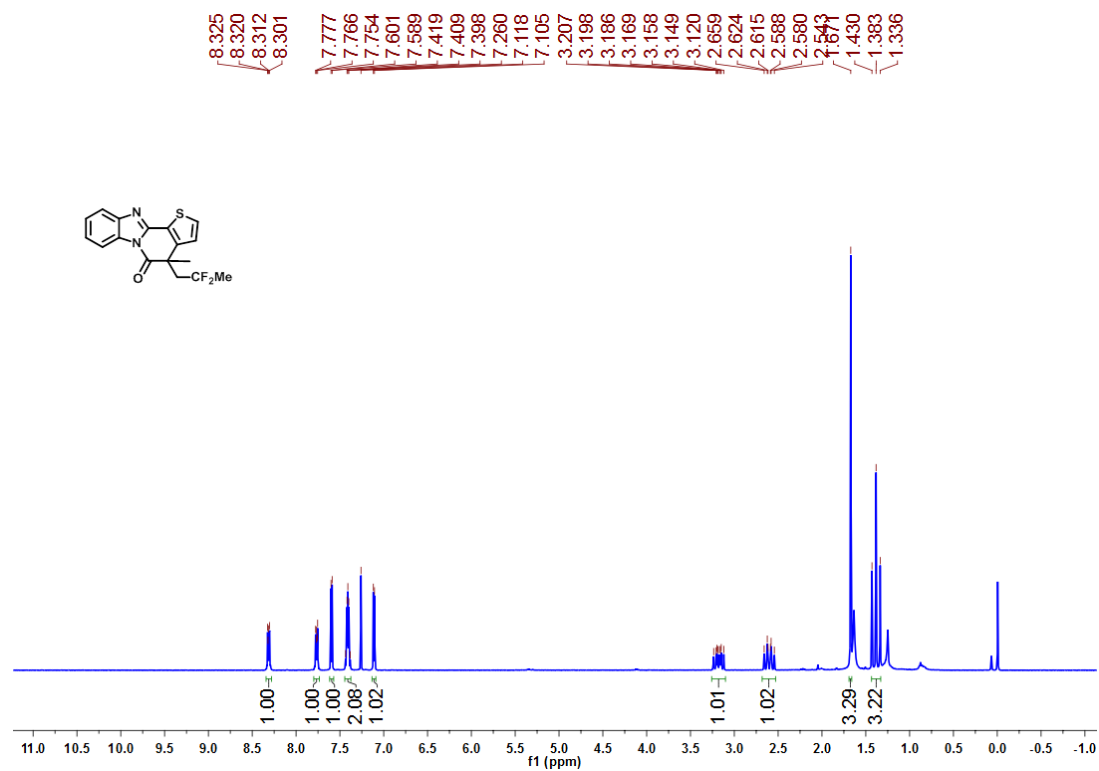
3u-¹³C{¹H} NMR (100 MHz, CDCl₃)



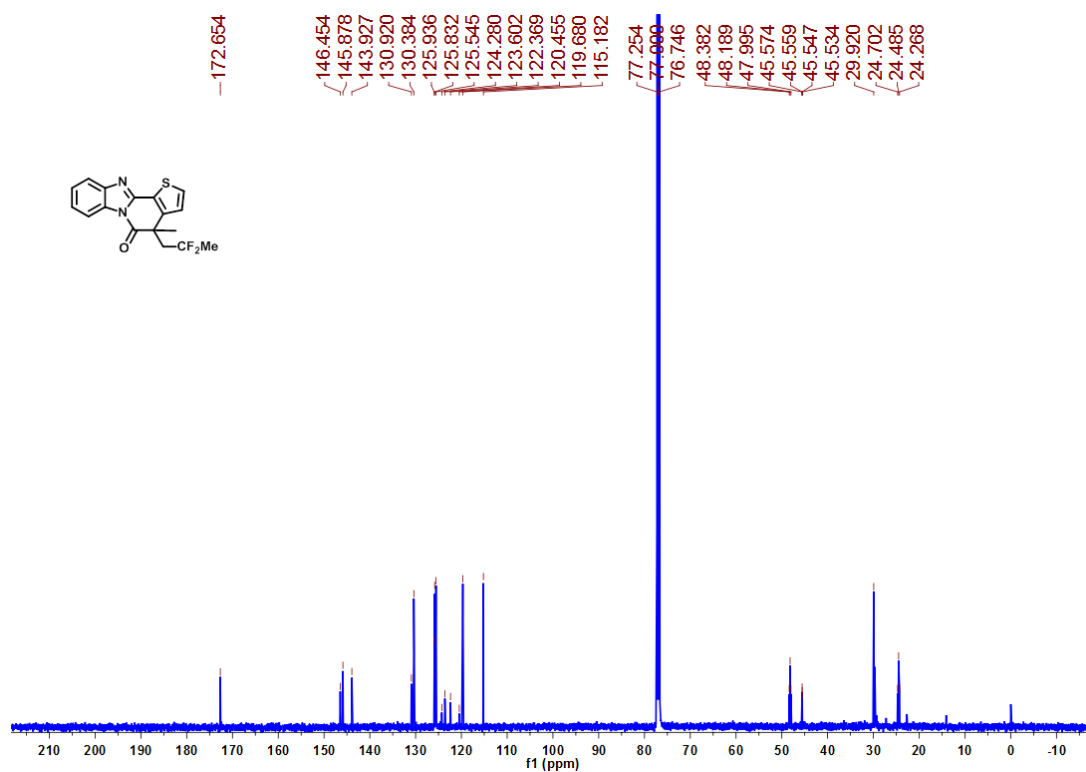
3u-¹⁹F NMR (471 MHz, CDCl₃)



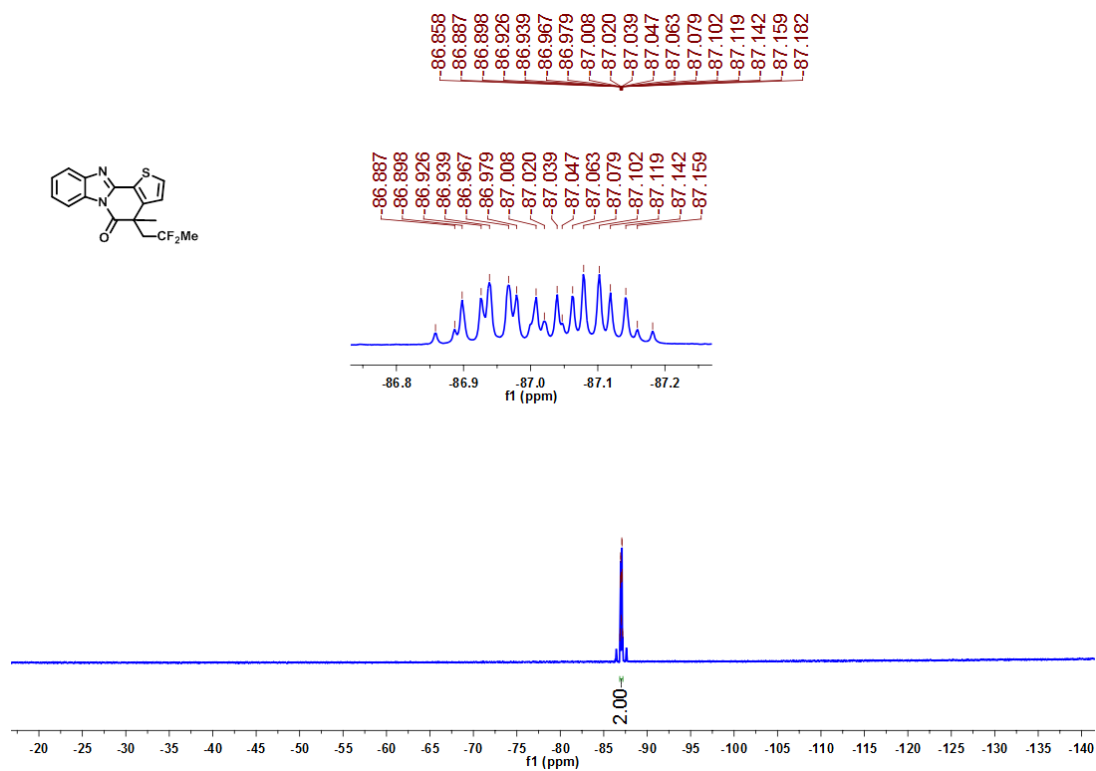
3v-¹H NMR (400 MHz, CDCl₃)



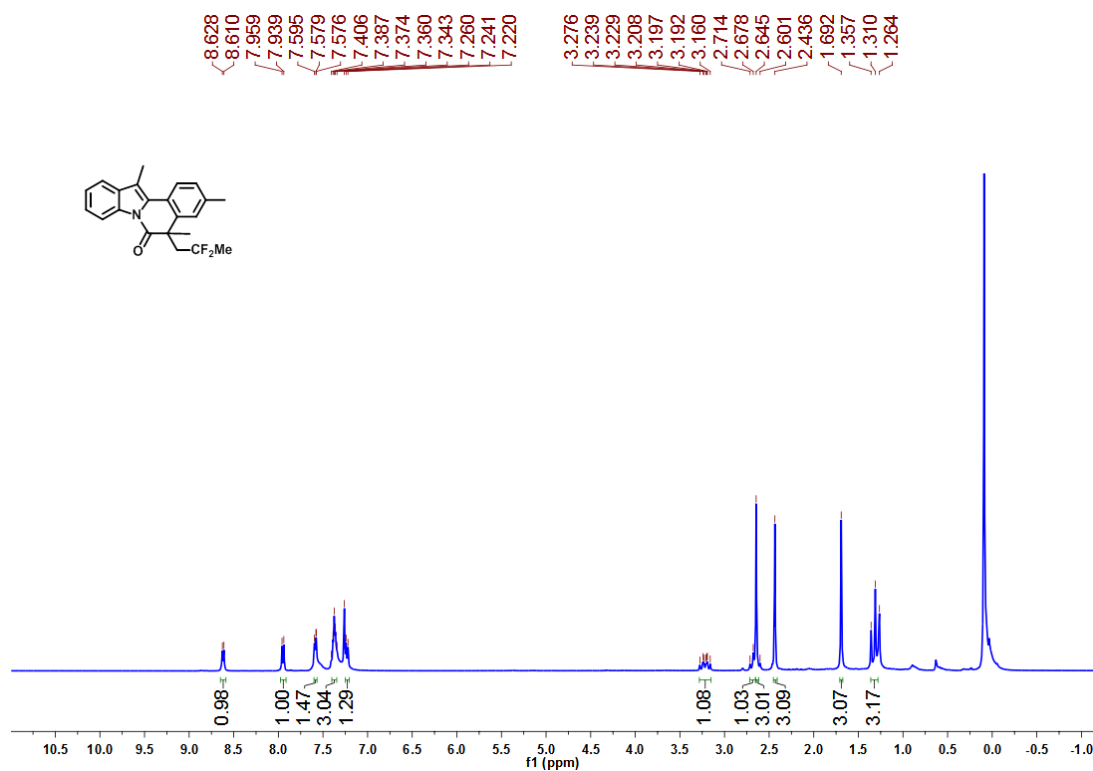
3v- $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3)



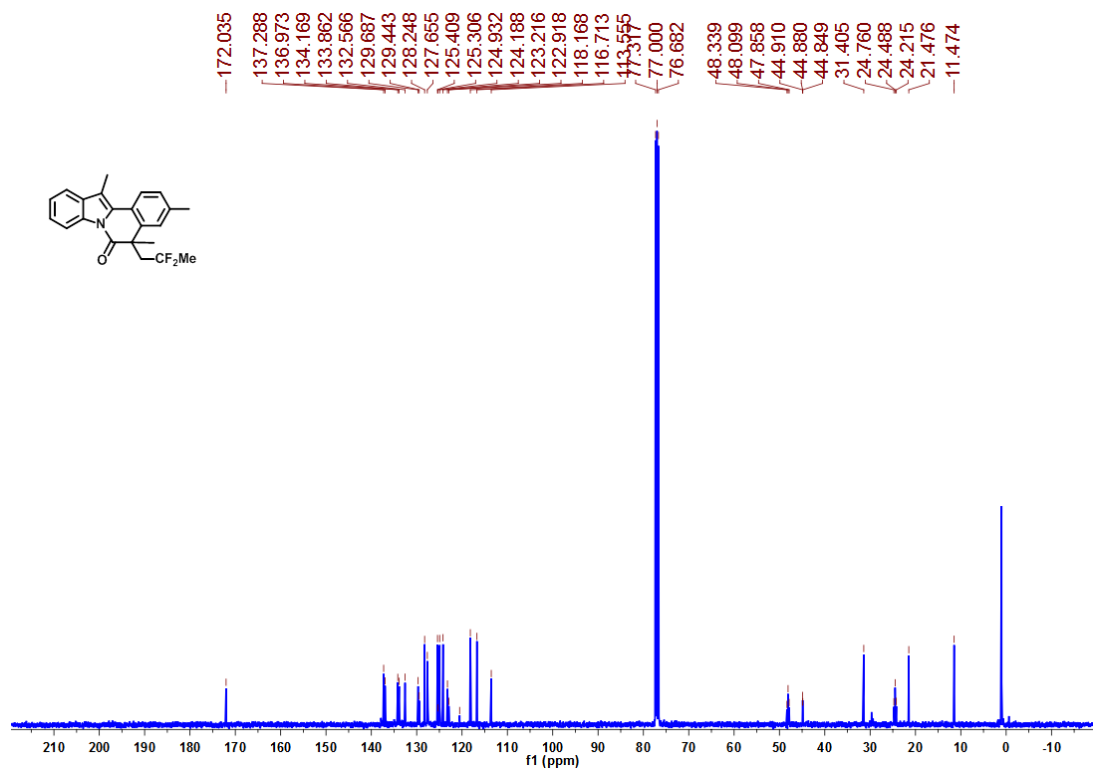
3v- ^{19}F NMR (471 MHz, CDCl_3)



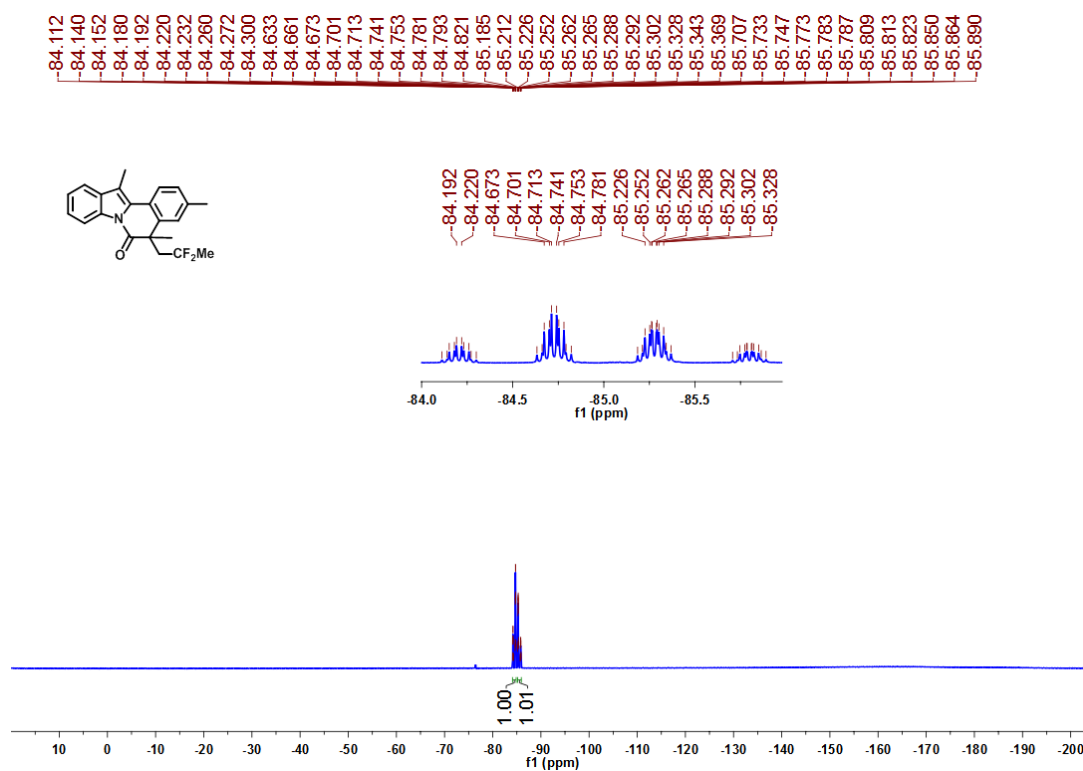
5a-¹H NMR (500 MHz, CDCl₃)



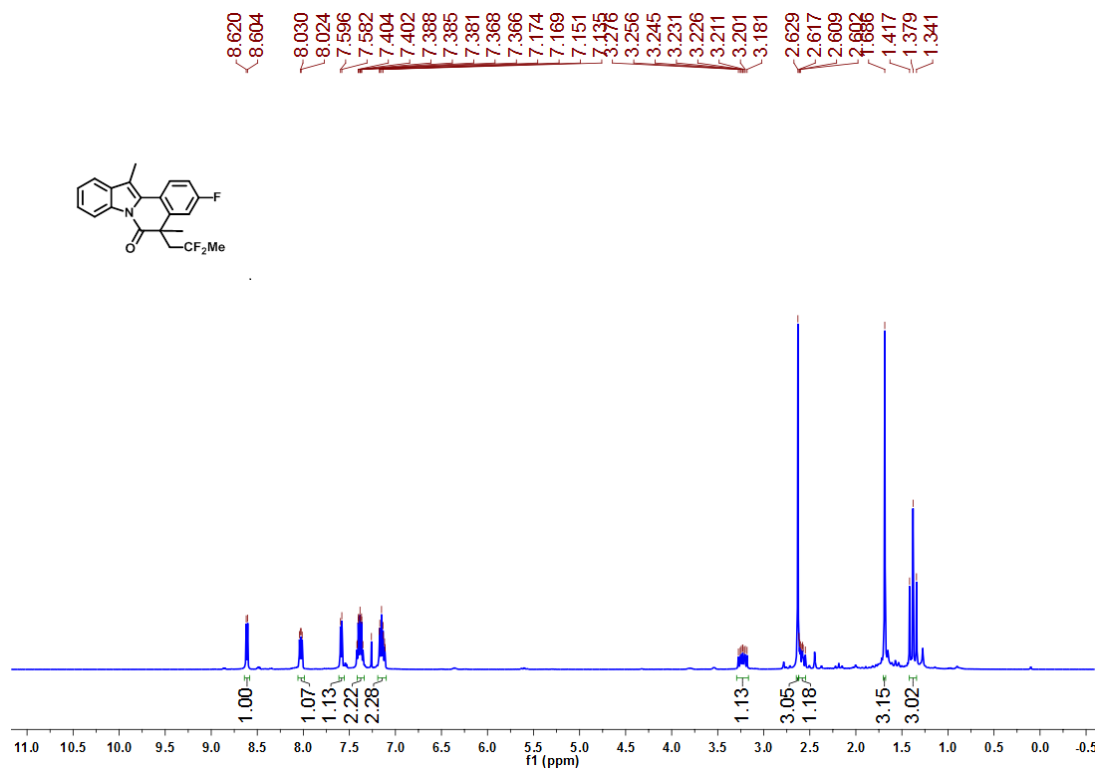
5a-¹³C{¹H} NMR (125 MHz, CDCl₃)



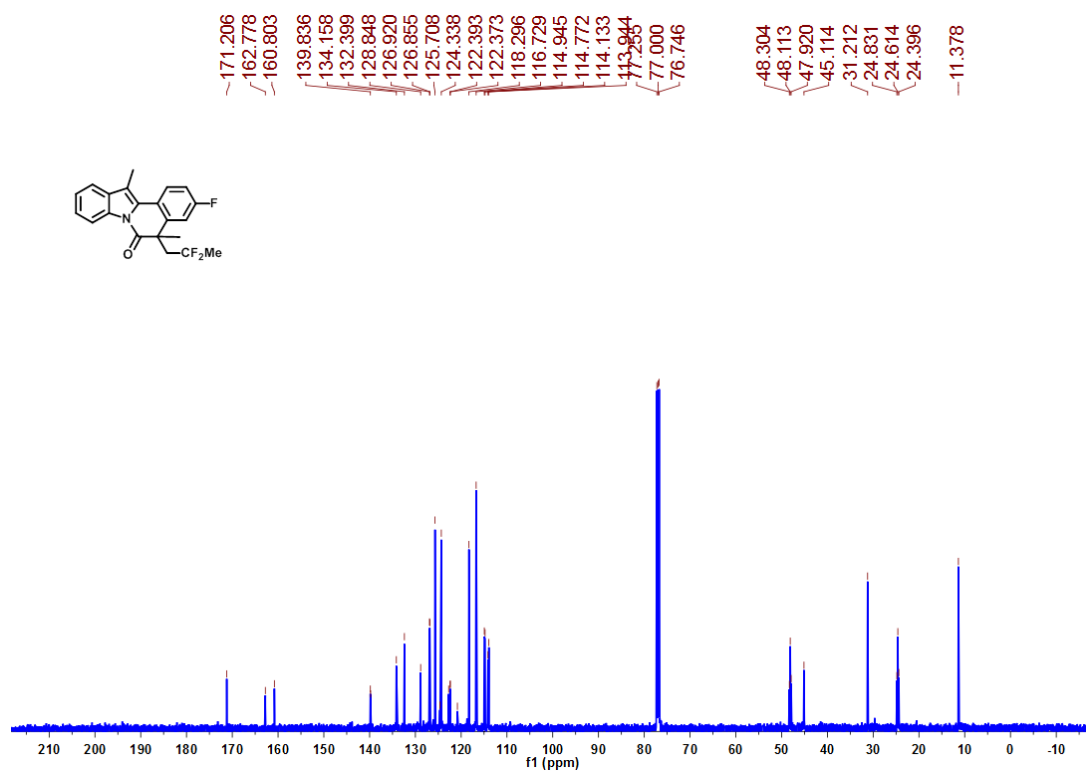
5a-¹⁹F NMR (471 MHz, CDCl₃)



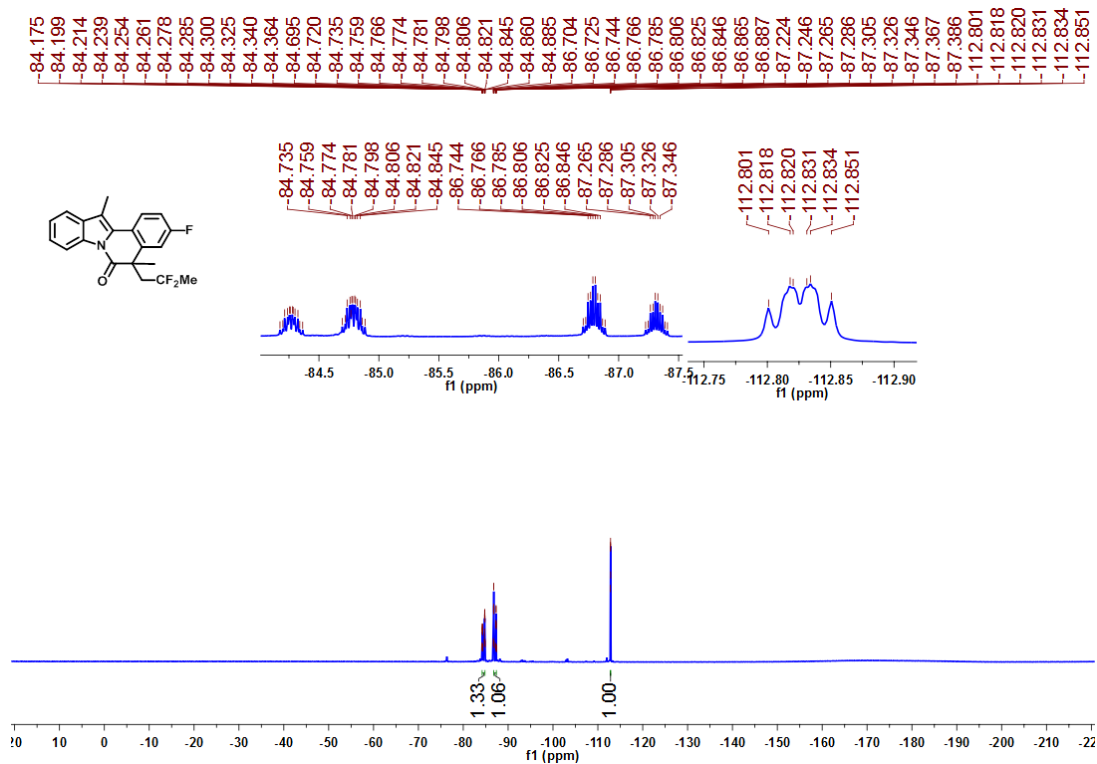
5b-¹H NMR (500 MHz, CDCl₃)



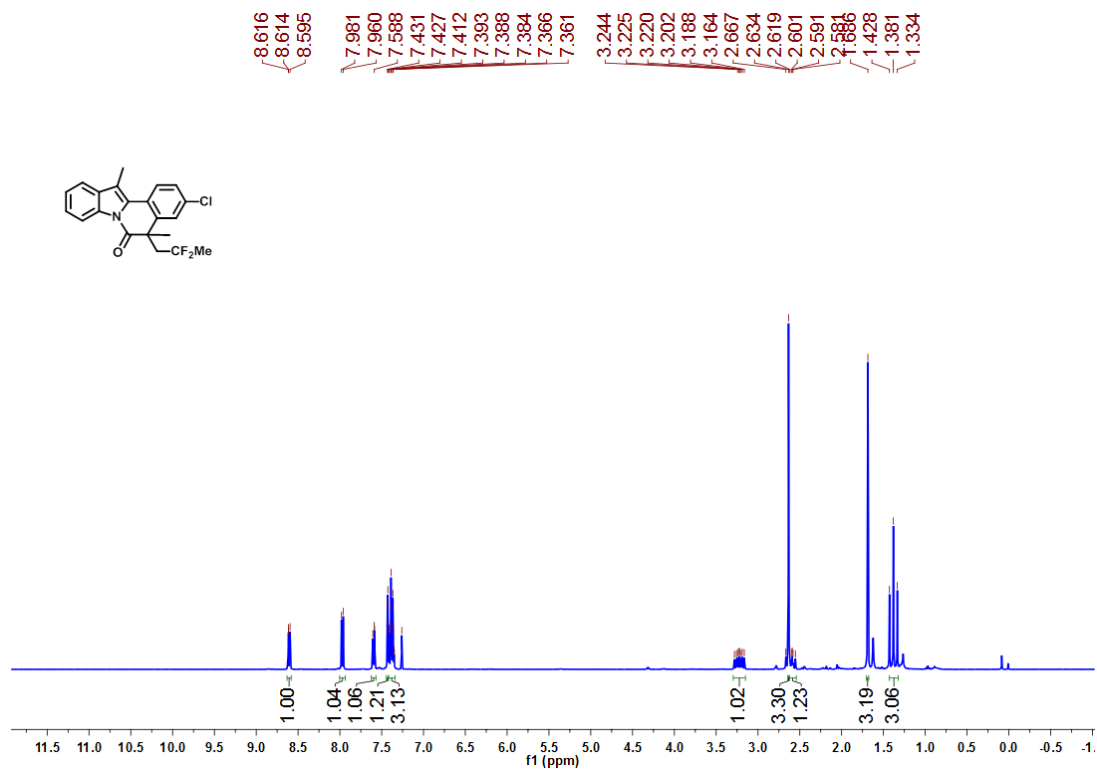
5b- $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3)



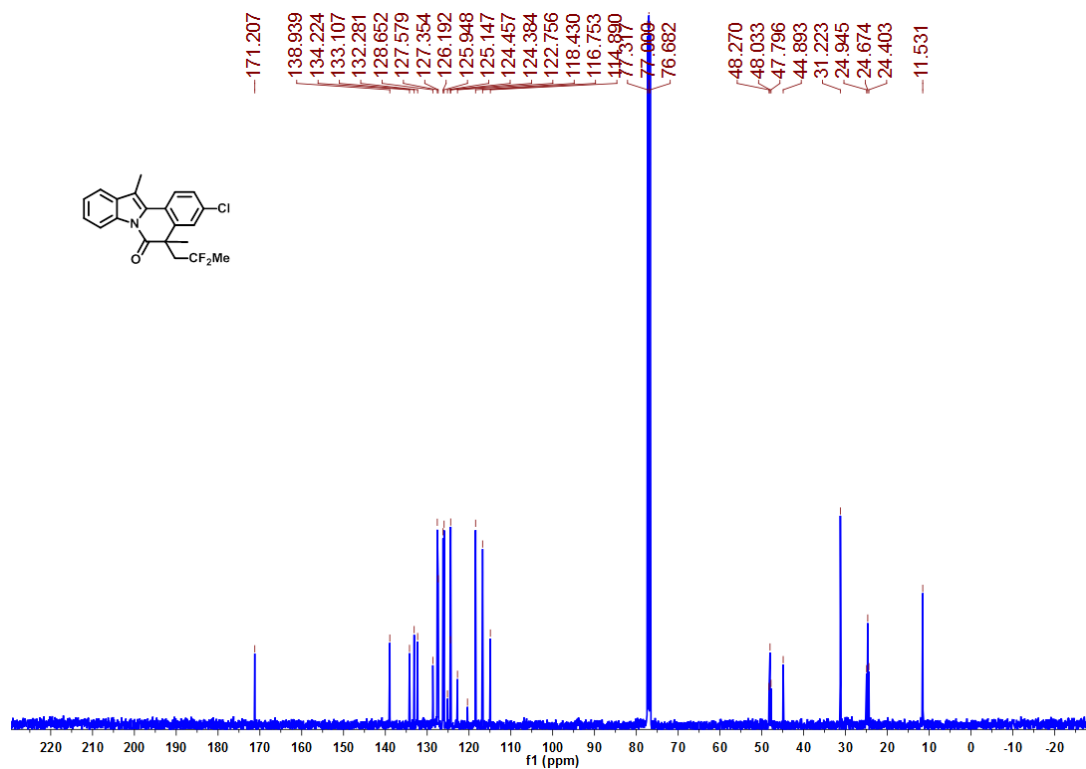
5b- ^{19}F NMR (471 MHz, CDCl_3)



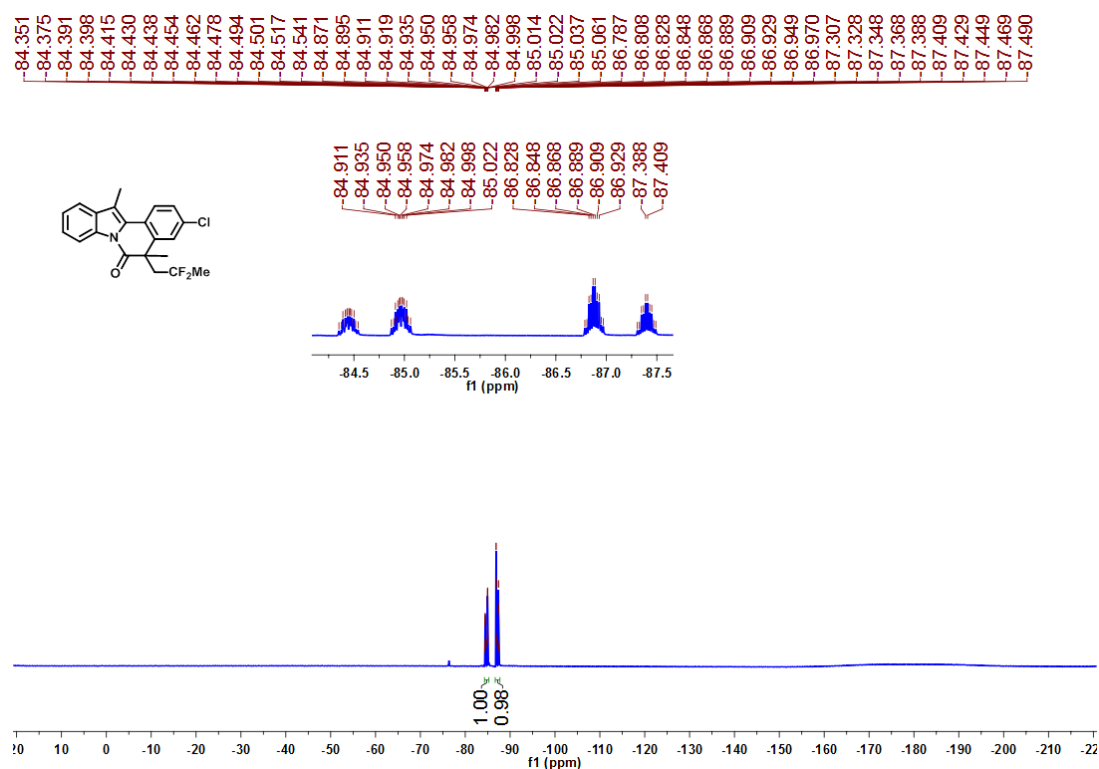
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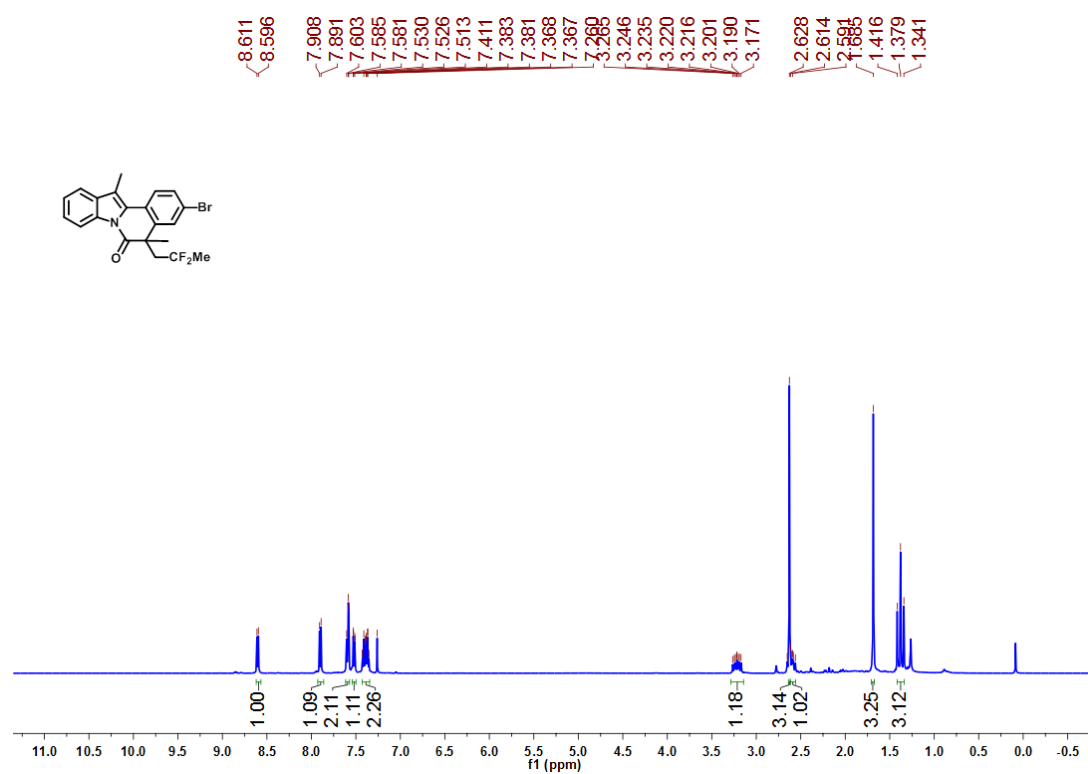
5c-¹³C{¹H} NMR (100 MHz, CDCl₃)



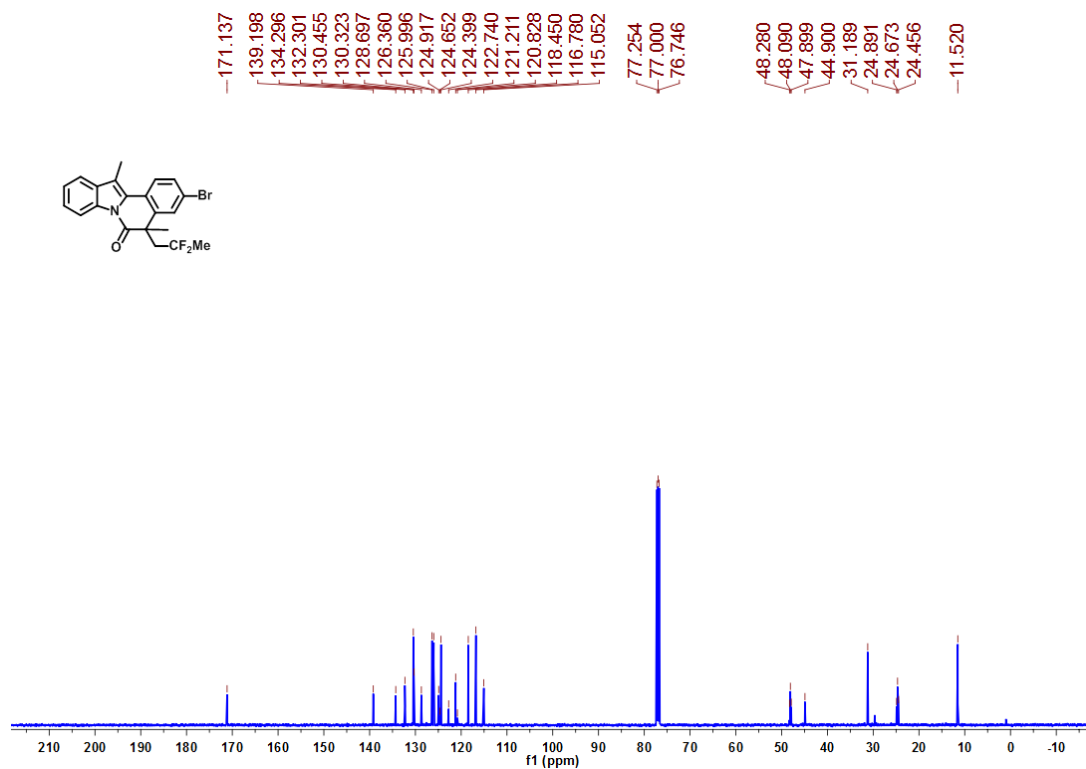
5c-¹⁹F NMR (471 MHz, CDCl₃)



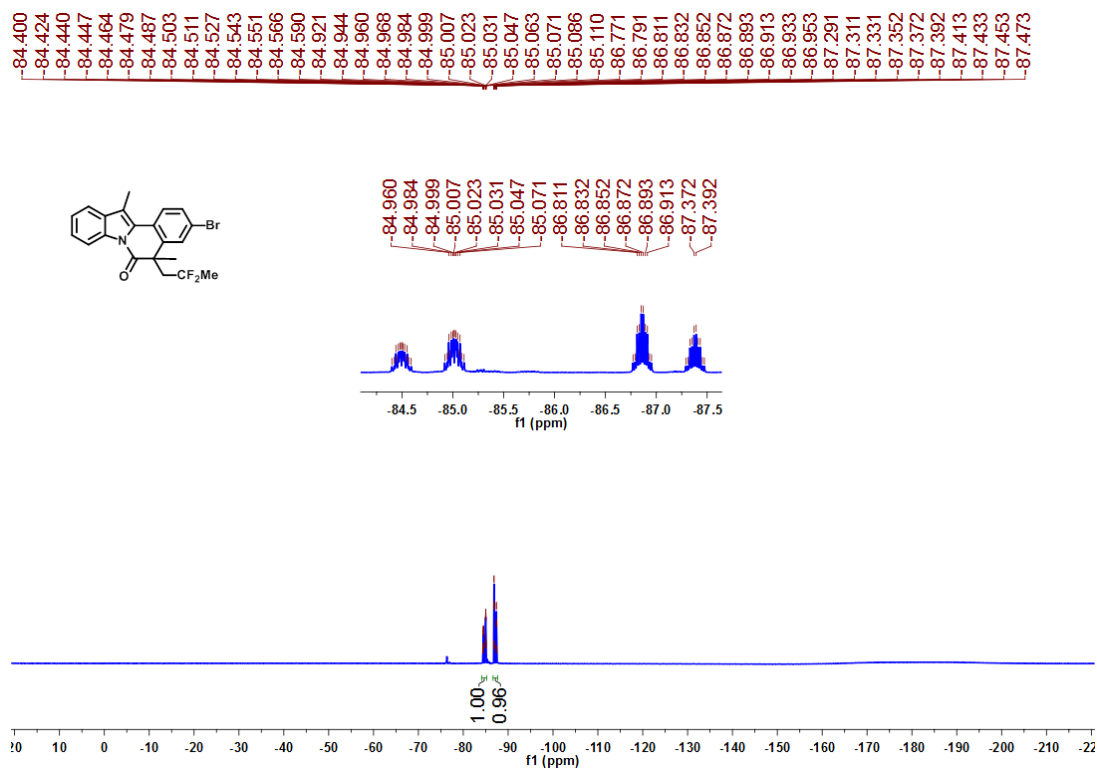
5d-¹H NMR (500 MHz, CDCl₃)



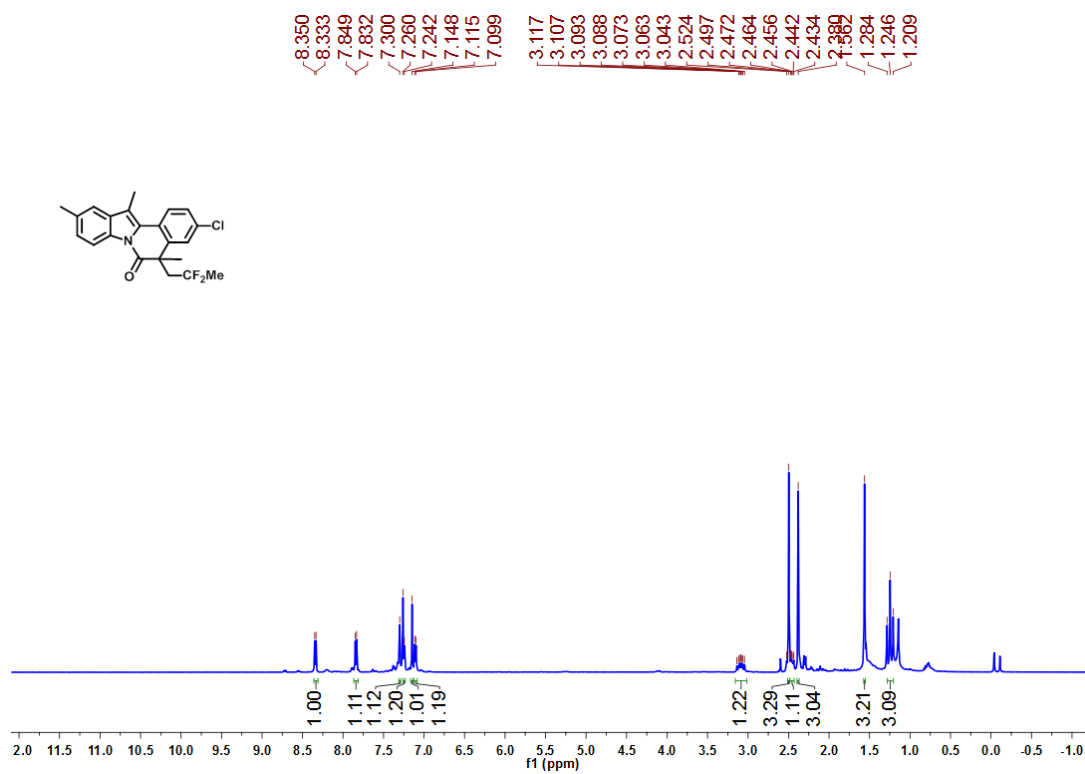
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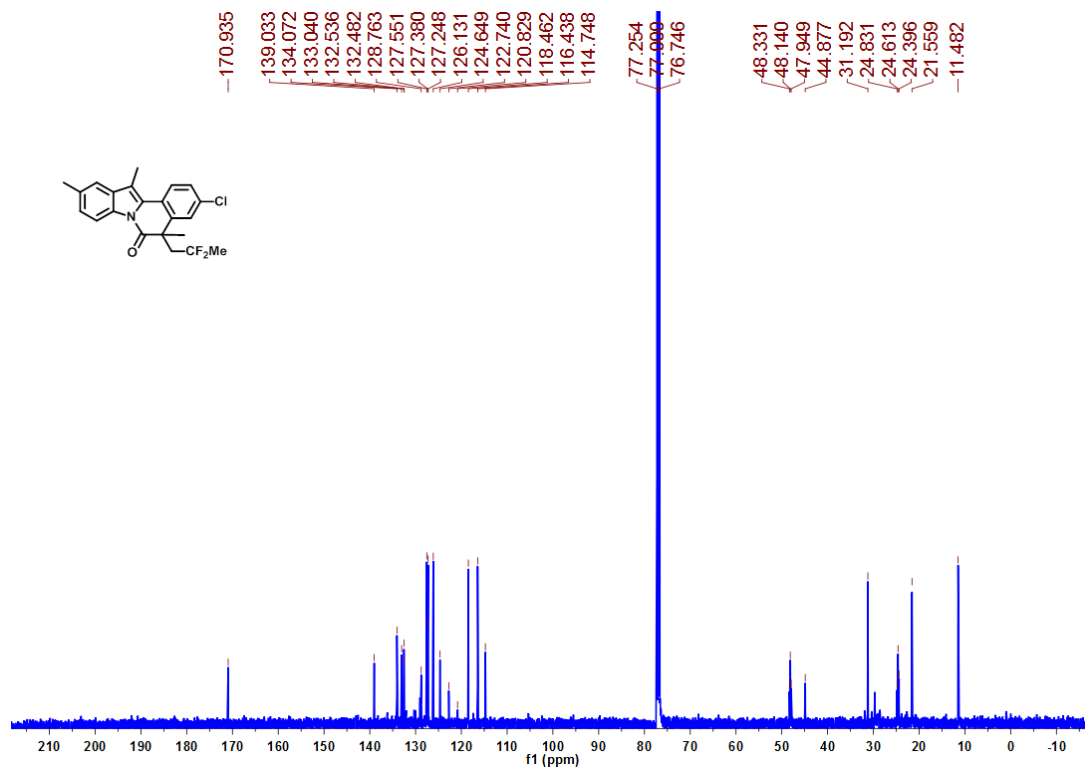
5d-¹⁹F NMR (471 MHz, CDCl₃)



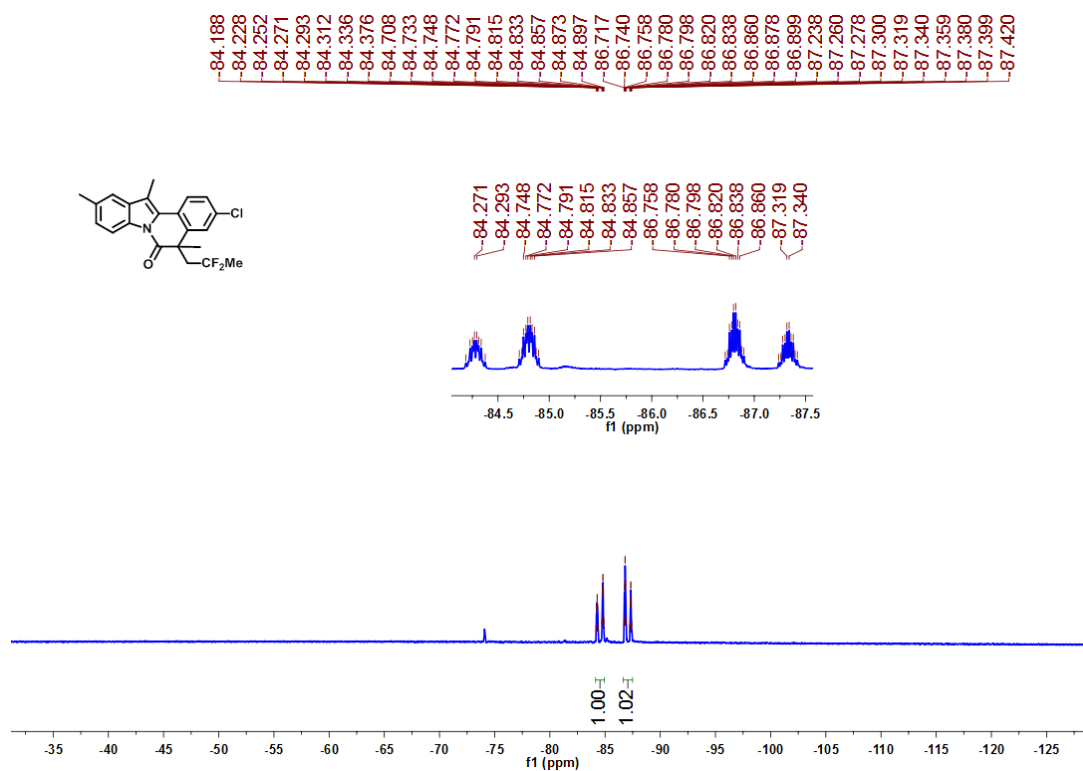
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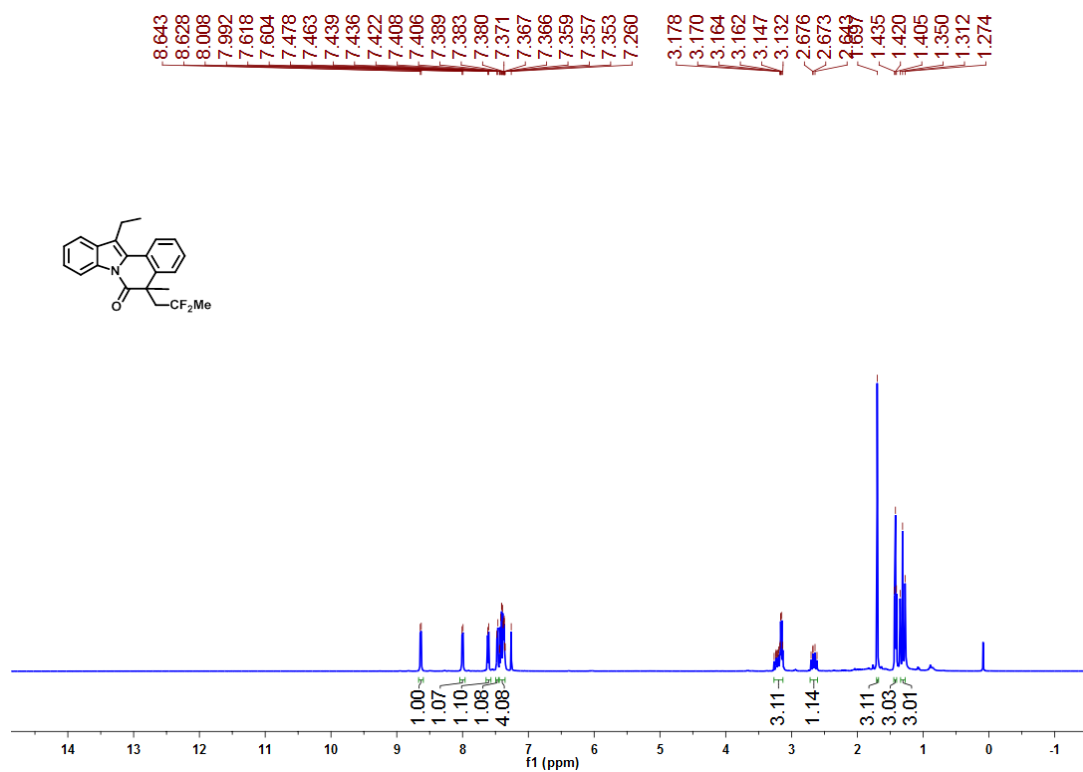
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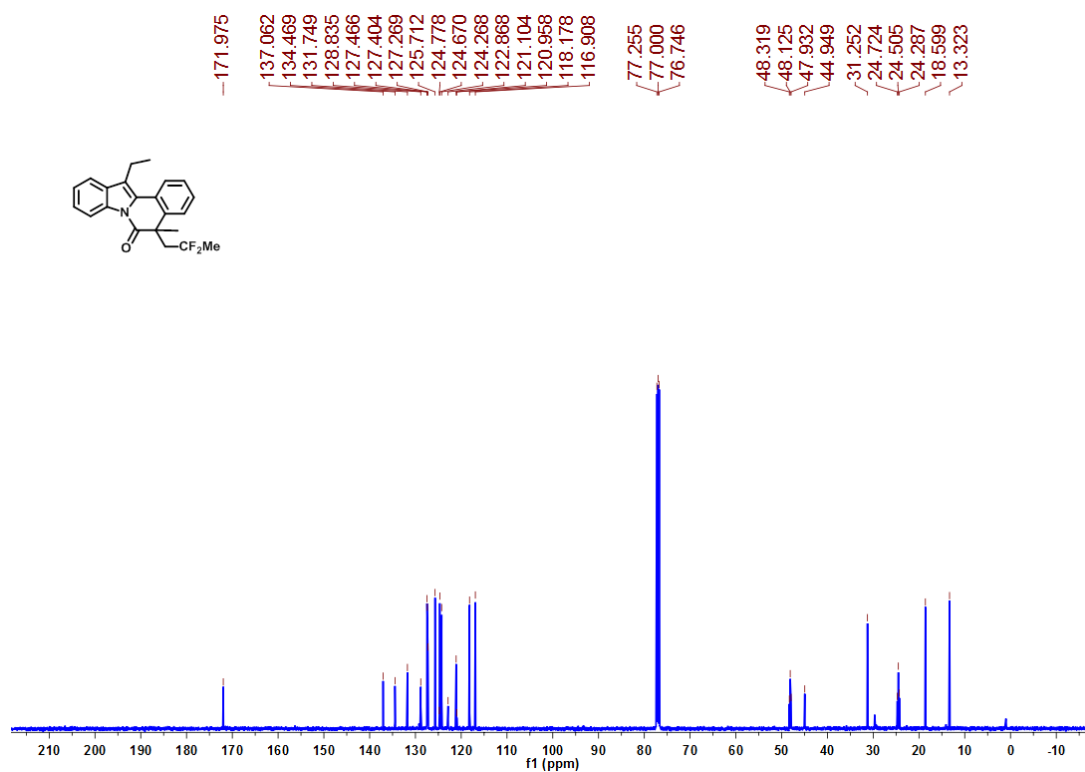
5e-¹⁹F NMR (471 MHz, CDCl₃)



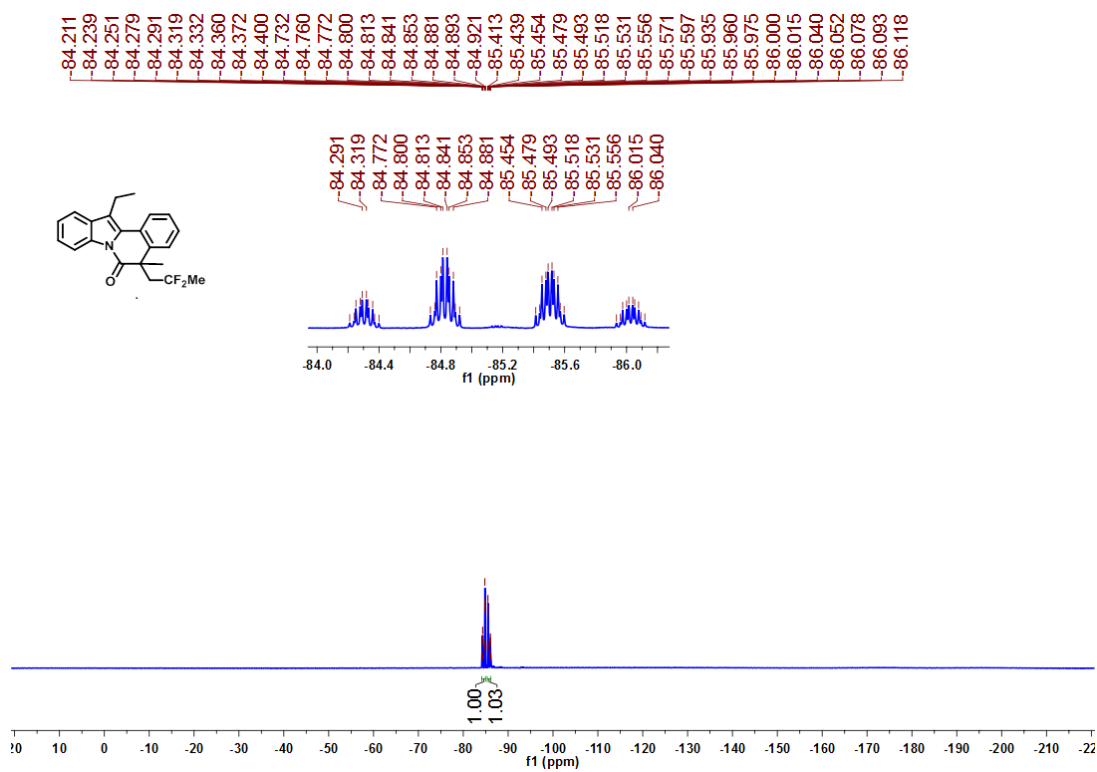
5f-¹H NMR (500 MHz, CDCl₃)



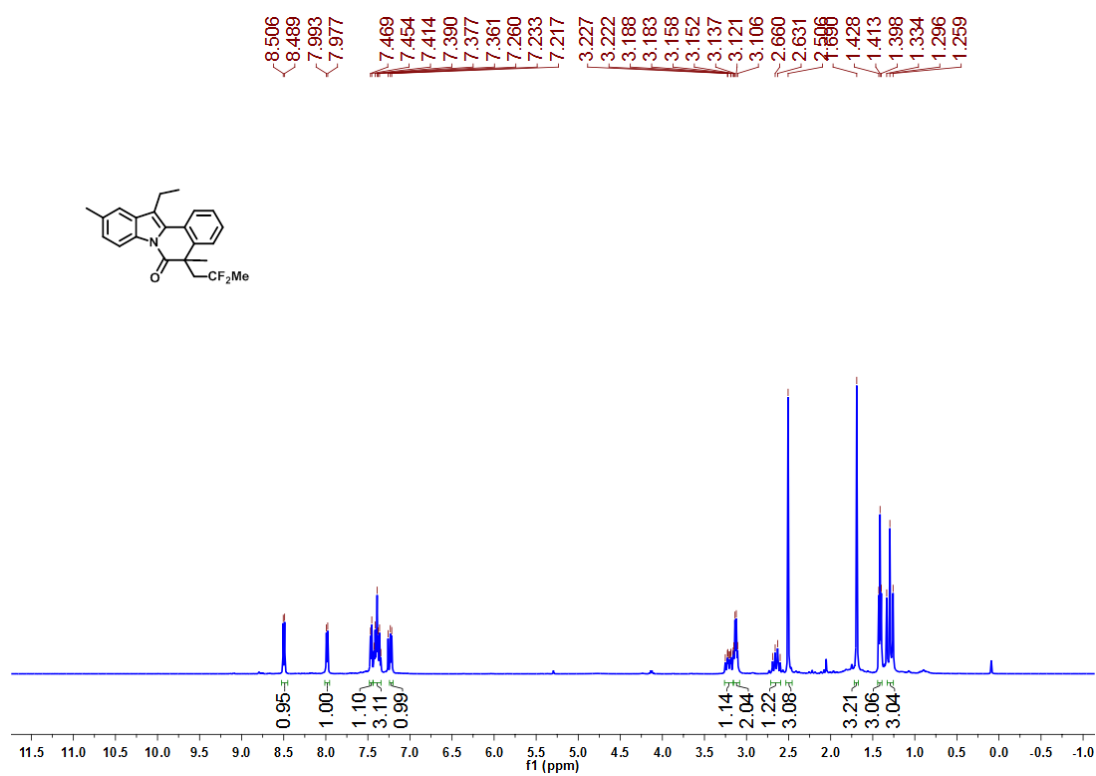
5f- $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3)



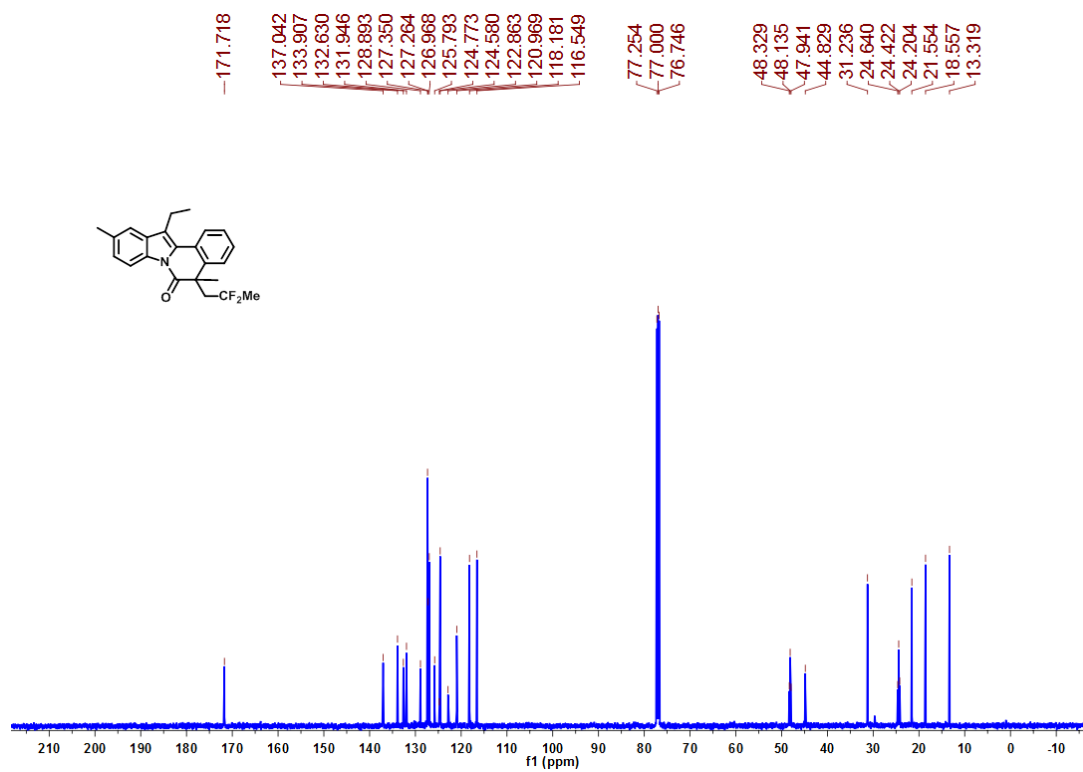
5f-¹⁹F NMR (471 MHz, CDCl₃)



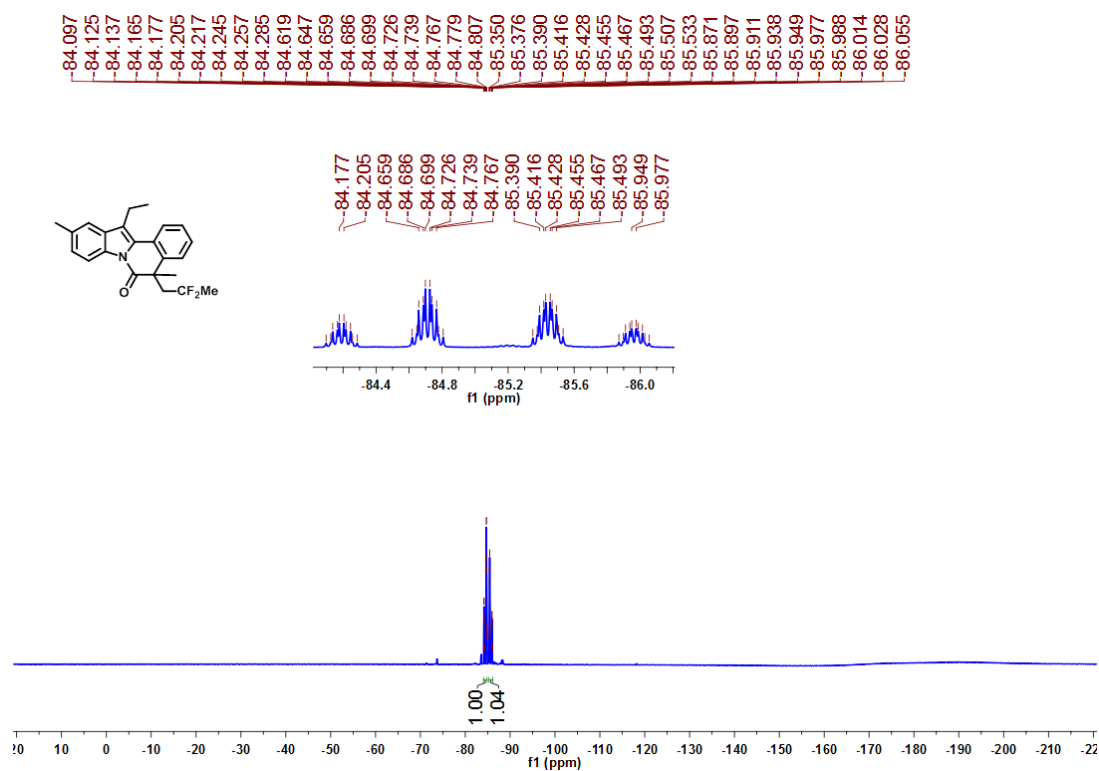
5g-¹H NMR (500 MHz, CDCl₃)



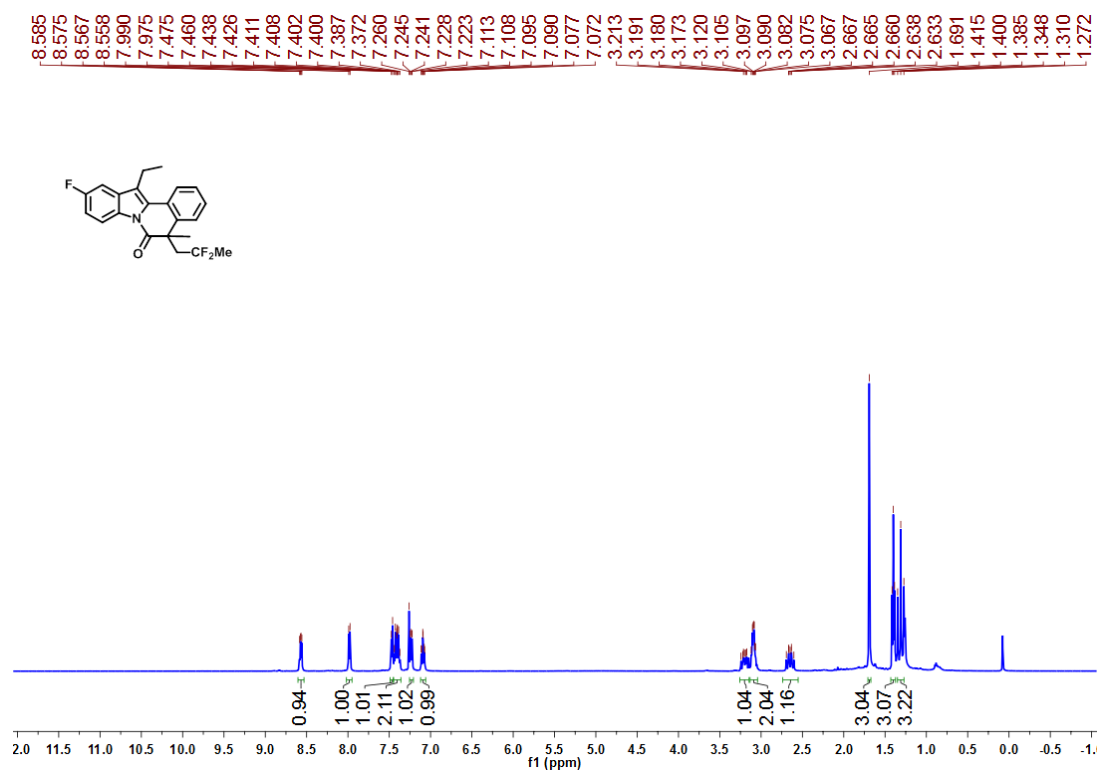
5g-¹³C{¹H} NMR (125 MHz, CDCl₃)



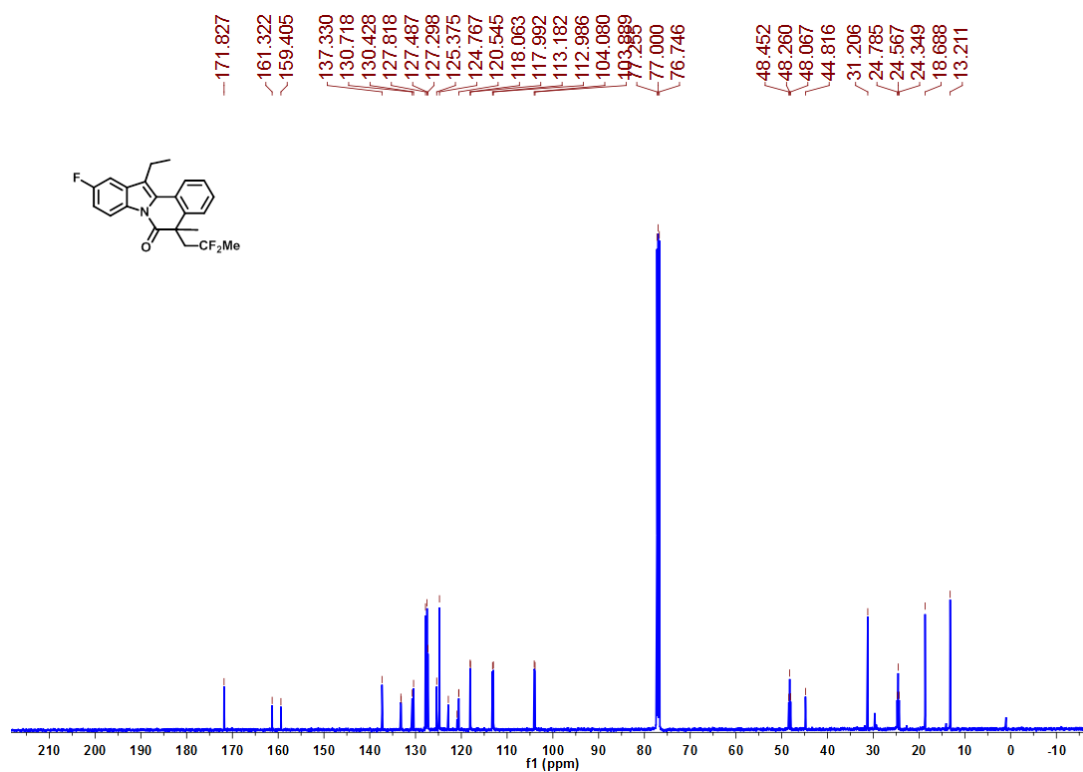
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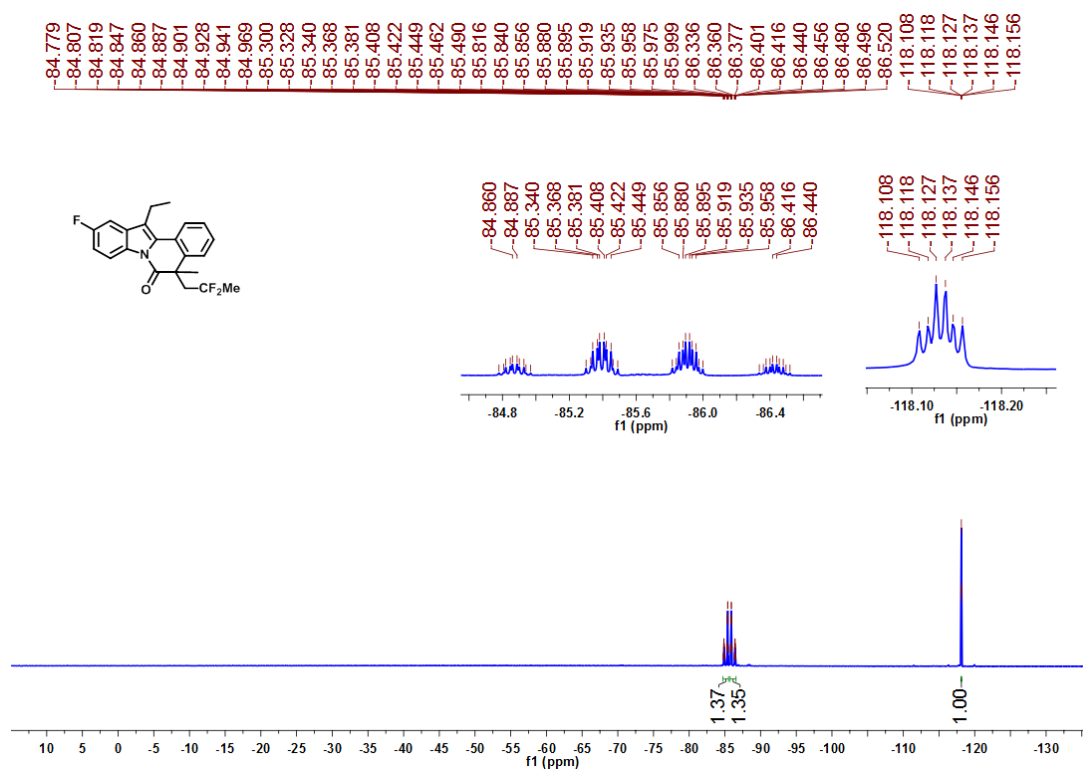
5h-¹H NMR (500 MHz, CDCl₃)



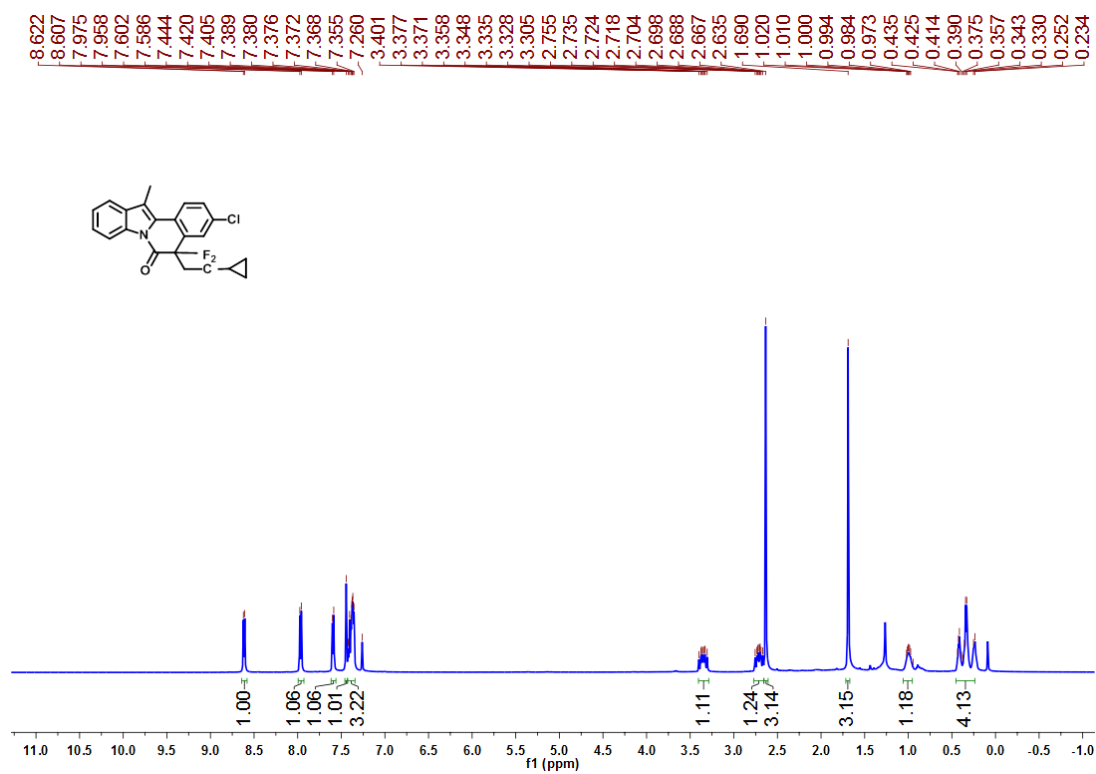
5h- $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3)



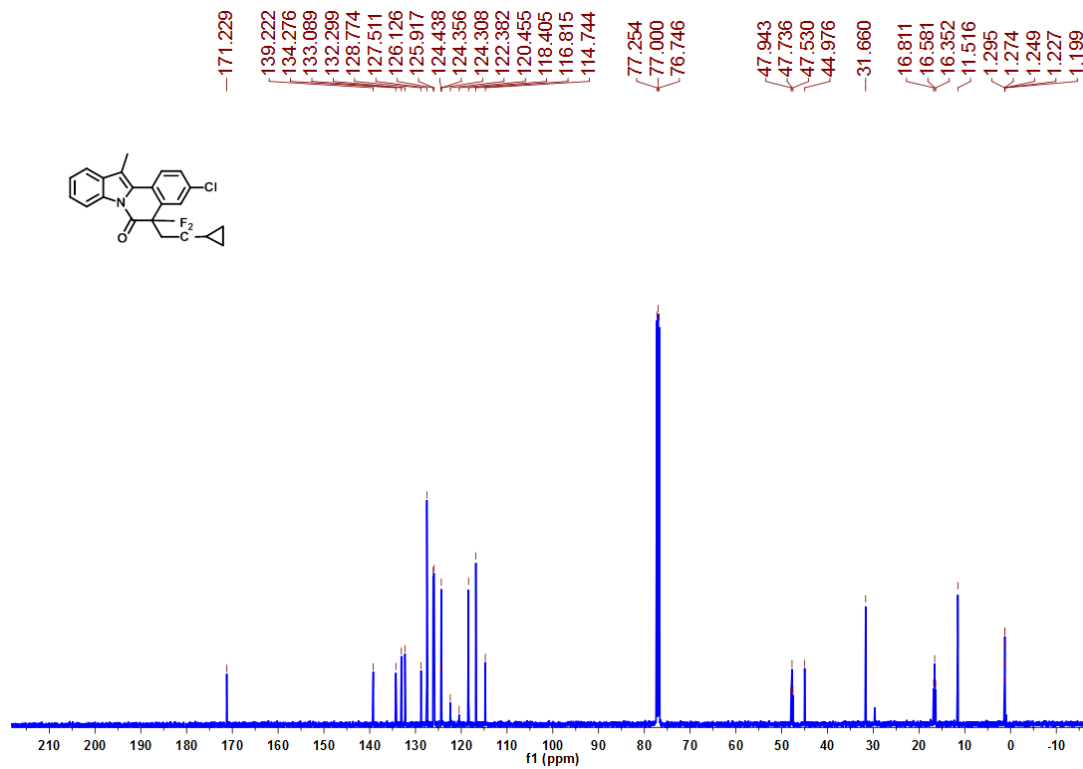
5h- ^{19}F NMR (471 MHz, CDCl_3)



5i- ^1H NMR (500 MHz, CDCl_3)



5i- $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3)



5i- ^{19}F NMR (471 MHz, CDCl_3)

