

Supporting Information

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

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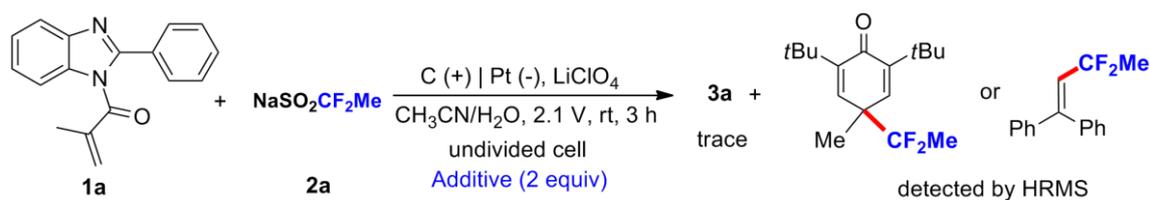
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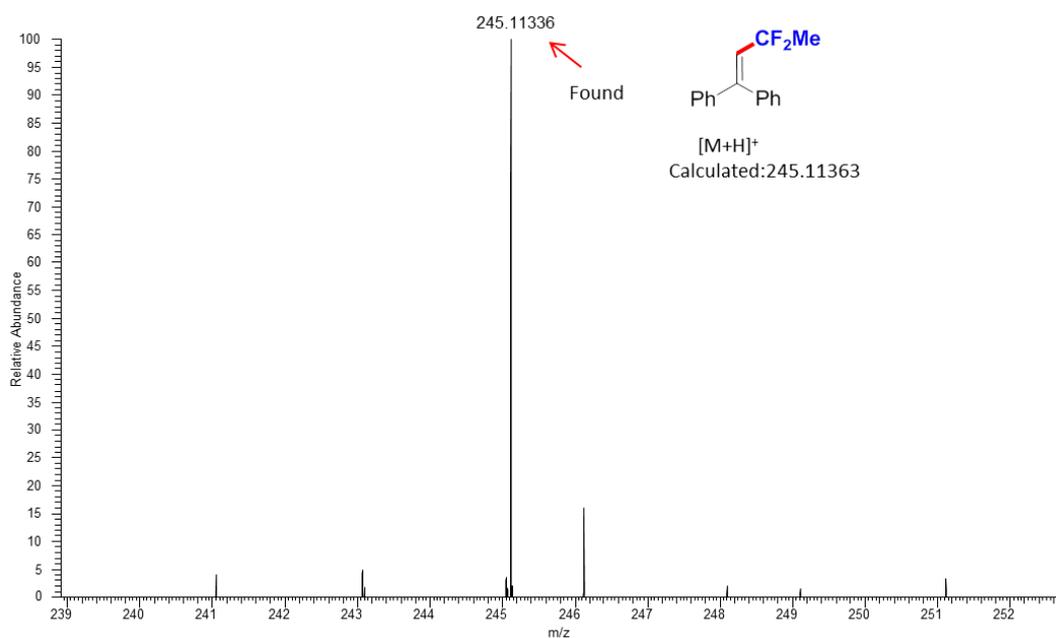
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1. Radical capturing experiments



To a 20 mL test tube with a stir bar was charged with, 2-arylbenzimidazoles (1 equiv., 0.2 mmol), MeCF₂SO₂Na, or sodium cyclopropyldifluoromethylsulfinate (3 equiv., 0.6 mmol), LiClO₄ (0.3 M), MeCN (4.5 mL), H₂O (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 Na₂SO₄ 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]



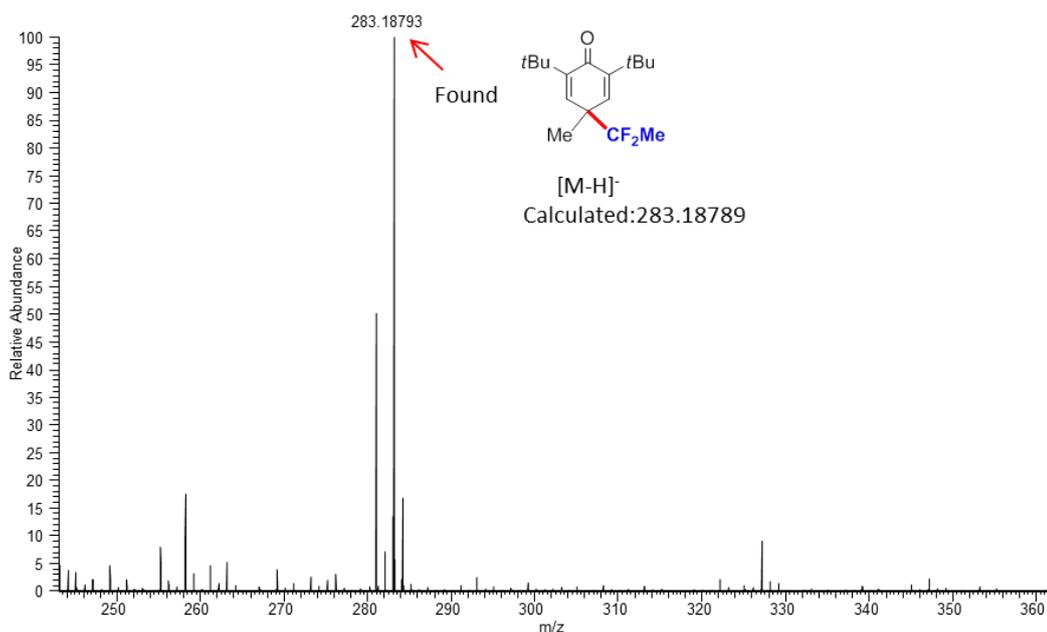


Figure S1. HRMS analysis of adduct products

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.

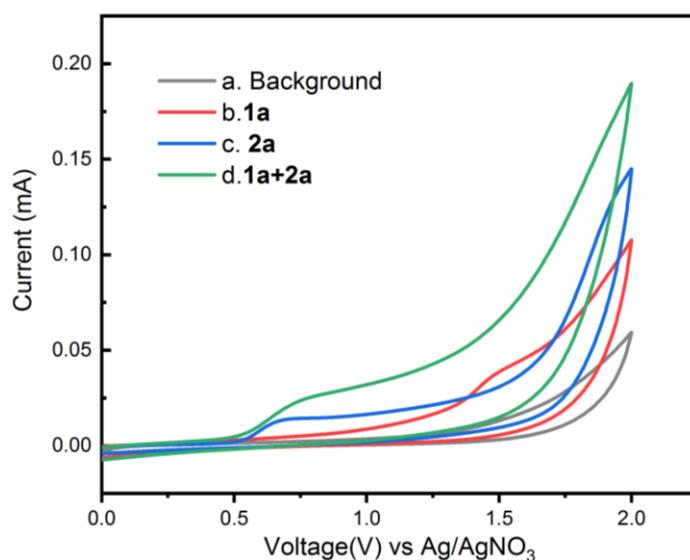


Figure S2. Cyclic voltammograms of substrates: (a) Background (0.1 M LiClO₄ in CH₃CN/H₂O (10/1,

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

3. 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 C₁₉H₁₅BrF₂N₂O [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 ₂ N ₂ O
Formula weight	405.24
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	Pbca
<i>a</i> /Å	13.5964(9)
<i>b</i> /Å	13.6099(7)
<i>c</i> /Å	18.1837(8)
<i>α</i> /°	90
<i>β</i> /°	90
<i>γ</i> /°	90
Volume/Å ³	3364.8(3)
<i>Z</i>	8
<i>ρ</i> _{calc} (g·cm ⁻³)	1.600
<i>μ</i> (mm ⁻¹)	2.473
<i>F</i> (000)	1632.0
Crystal size/mm ³	0.29 × 0.28 × 0.23

Radiation	Mo K α ($\lambda = 0.71073$)
2 θ 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 / $e \text{ \AA}^{-3}$	0.40/-0.39
CCDC	2303467

Displacement ellipsoids are drawn at the 50% probability level

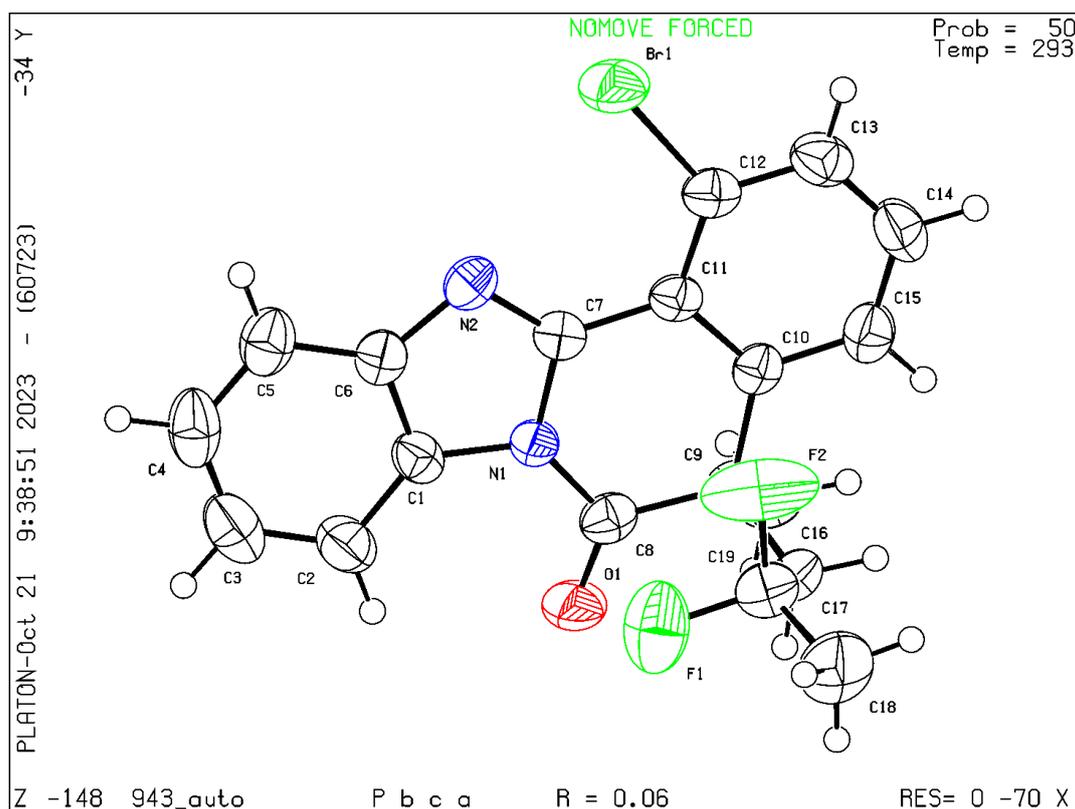


Fig. S3 Structure of product **3m**

4. 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 C₂₃H₂₀ClF₂NO [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 ₂ NO
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 [Rint = 0.0667, Rsigma = 0.0561]
Data/restraints/parameters	3873/0/255
Goodness-of-fit on F^2	1.037
Final R indexes [$I \geq 2\sigma(I)$]	$R1 = 0.0460$, $wR2 = 0.1122$
Final R indexes [all data]	$R1 = 0.0596$, $wR2 = 0.1214$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.30/-0.31
CCDC	2307007

Displacement ellipsoids are drawn at the 50% probability level

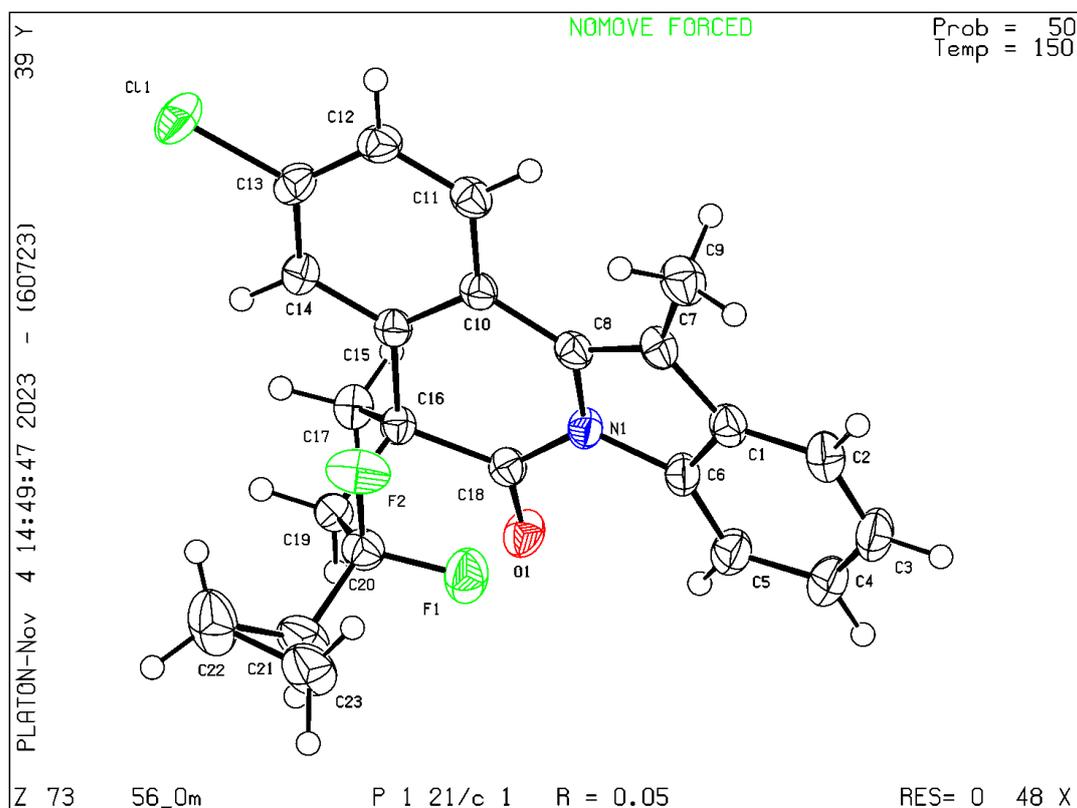
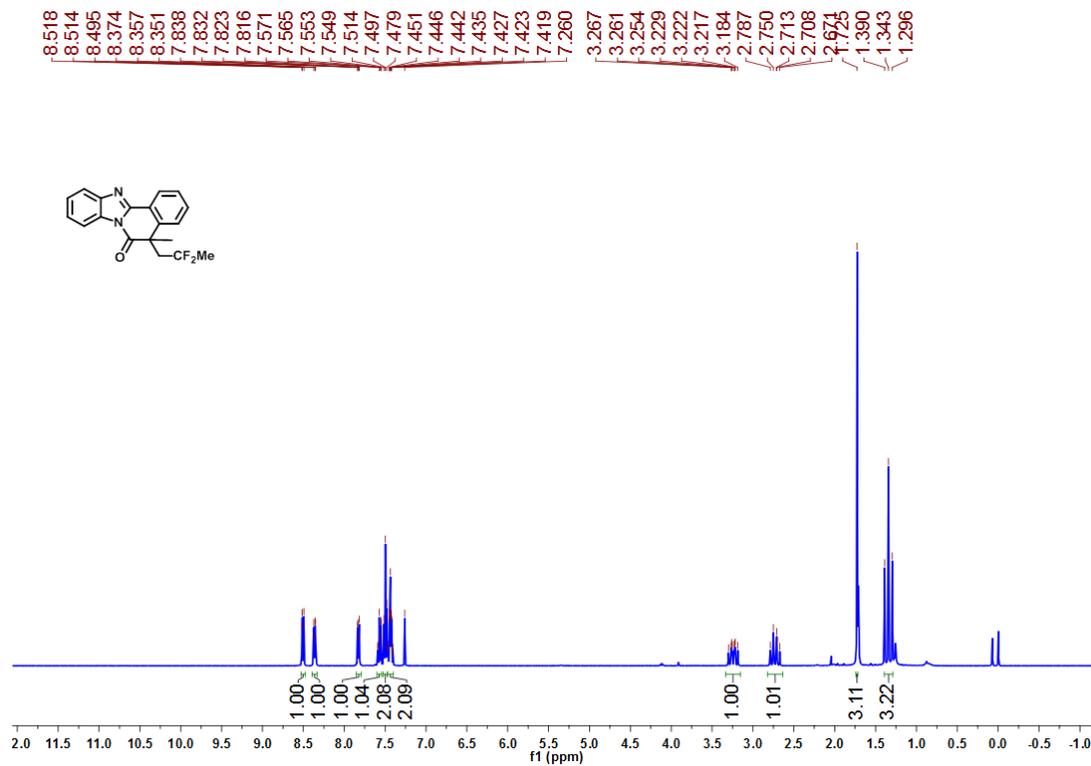


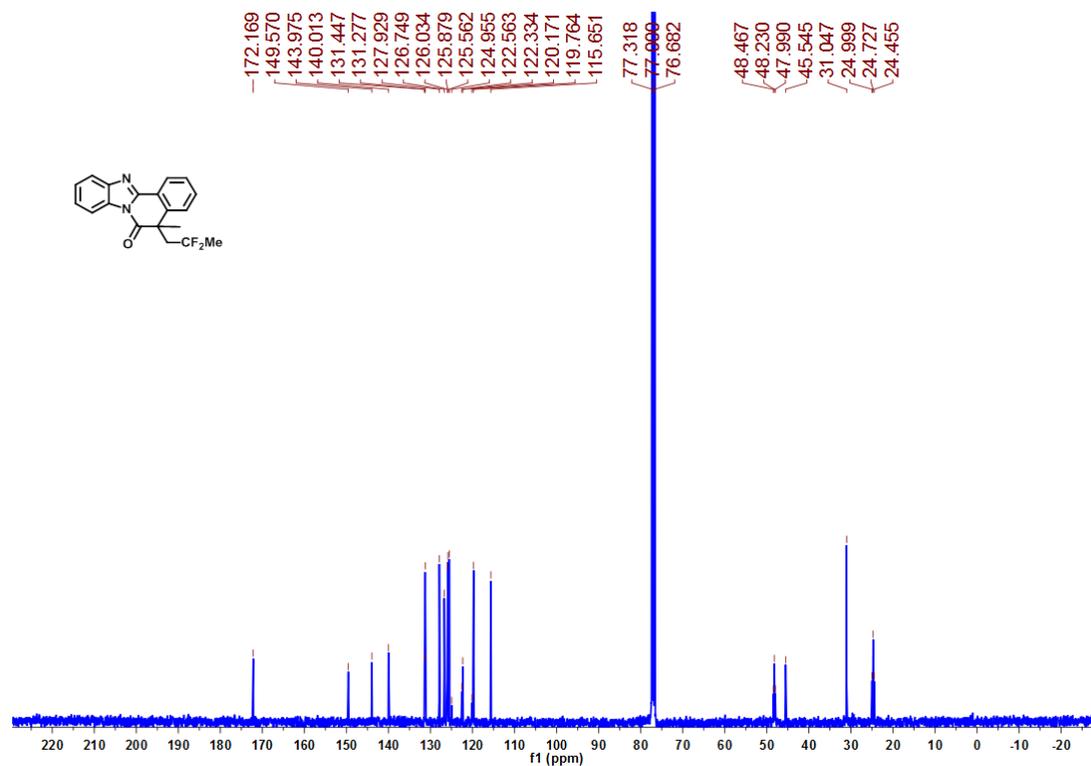
Fig. S4 Structure of product **5i**

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

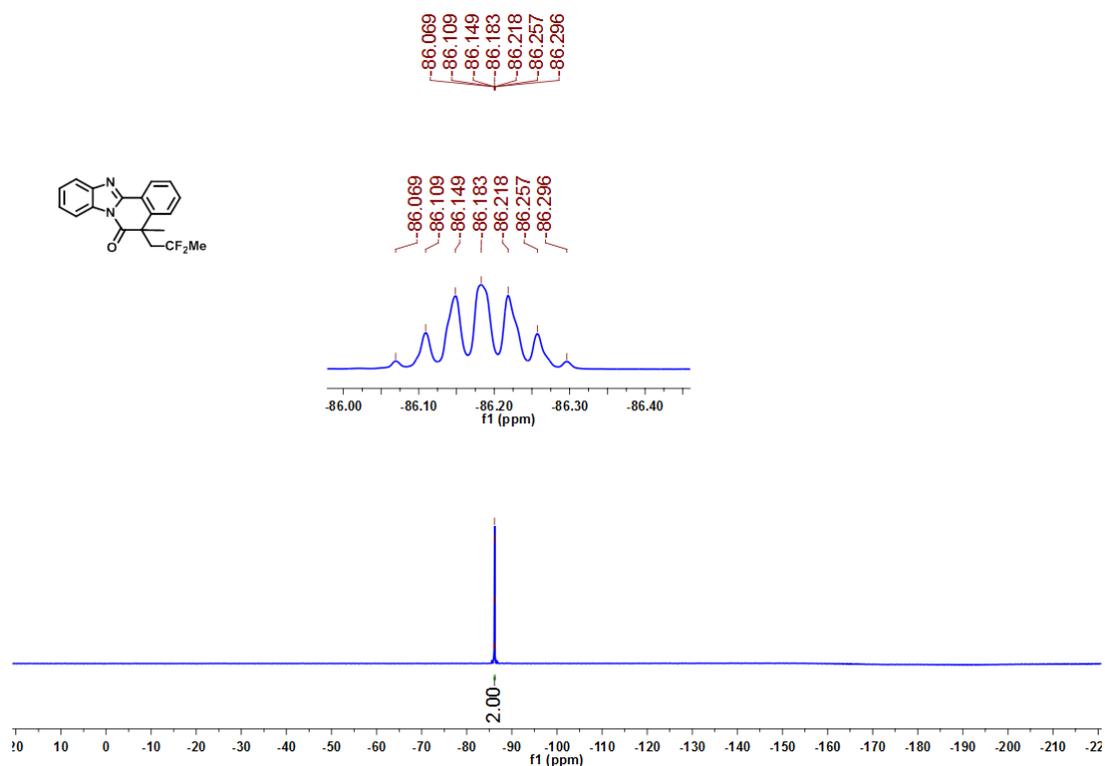
3a - ^1H NMR (400 MHz, CDCl_3)



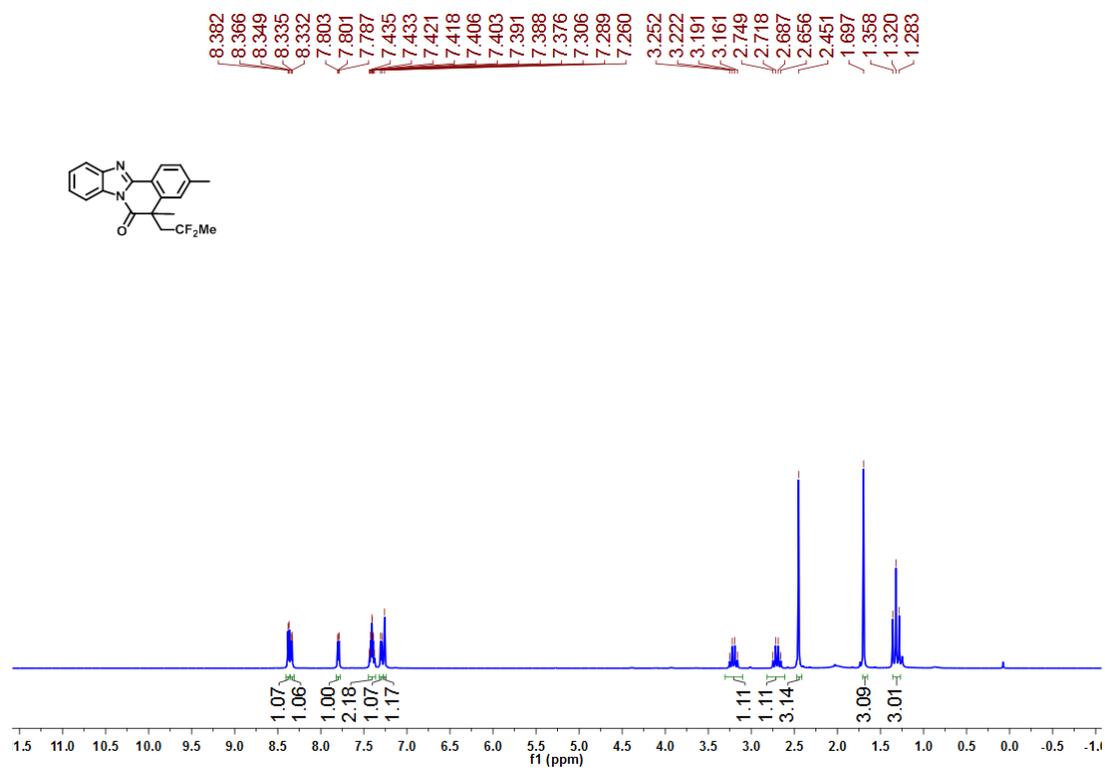
3a - $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3)



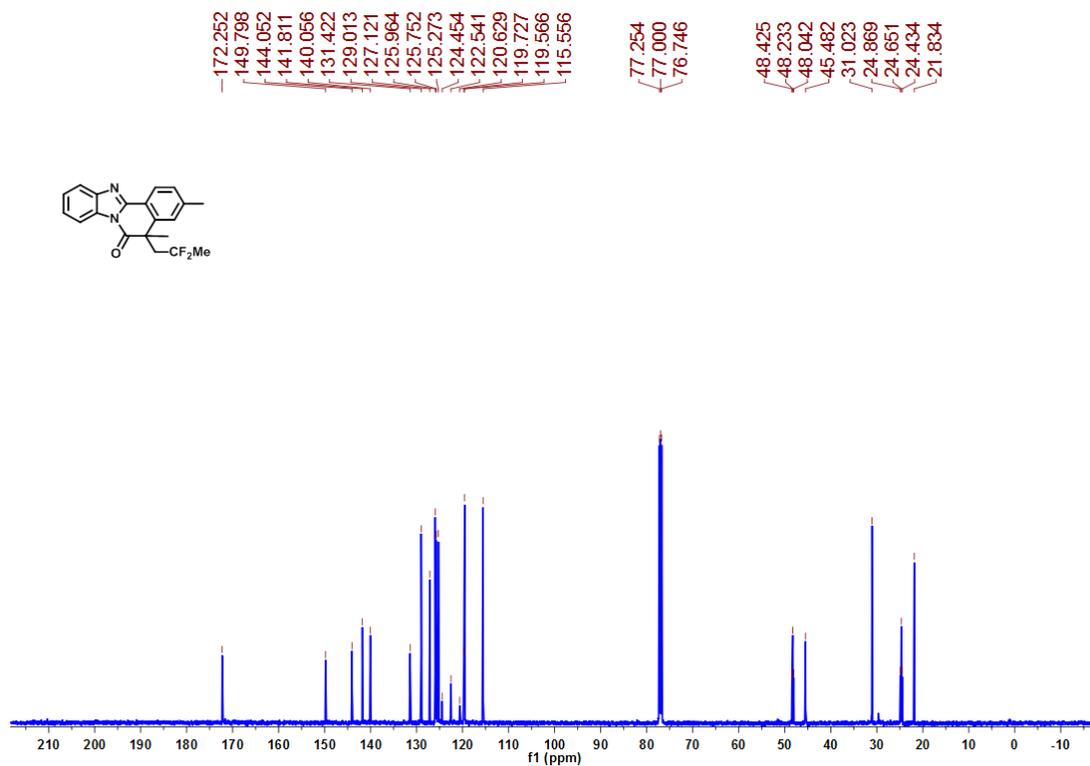
3a-¹⁹F NMR (471 MHz, CDCl₃)



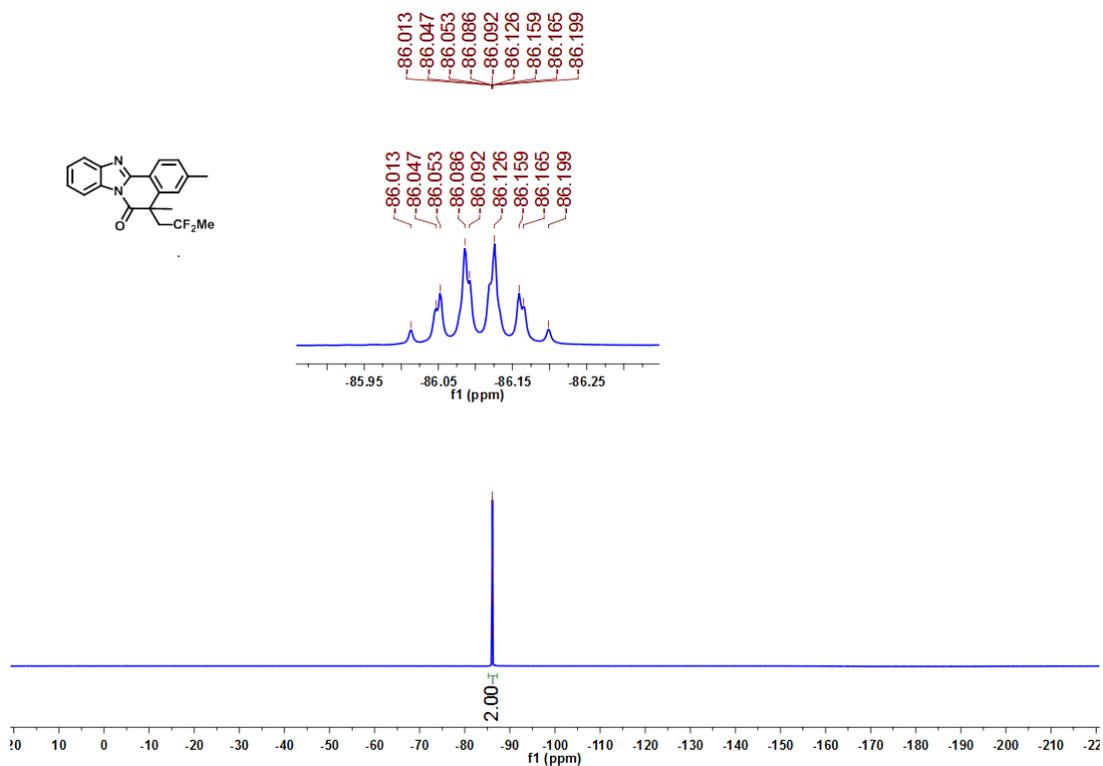
3b-¹H NMR (500 MHz, CDCl₃)



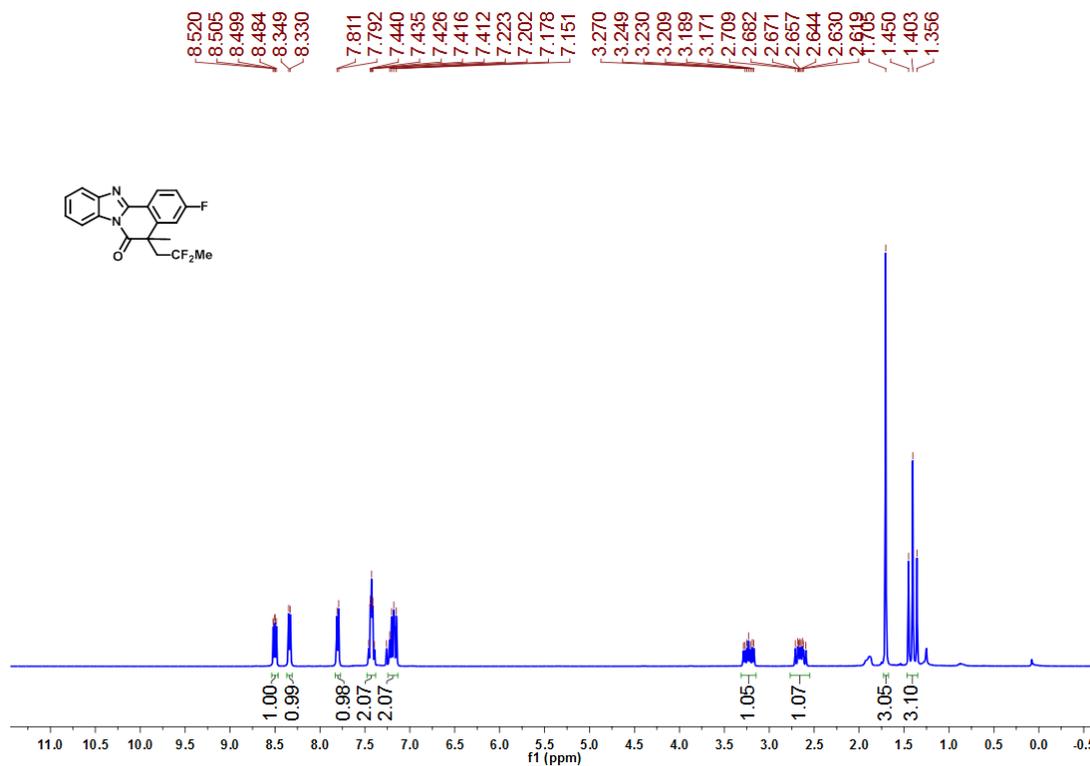
3b-¹³C{¹H} NMR (125 MHz, CDCl₃)



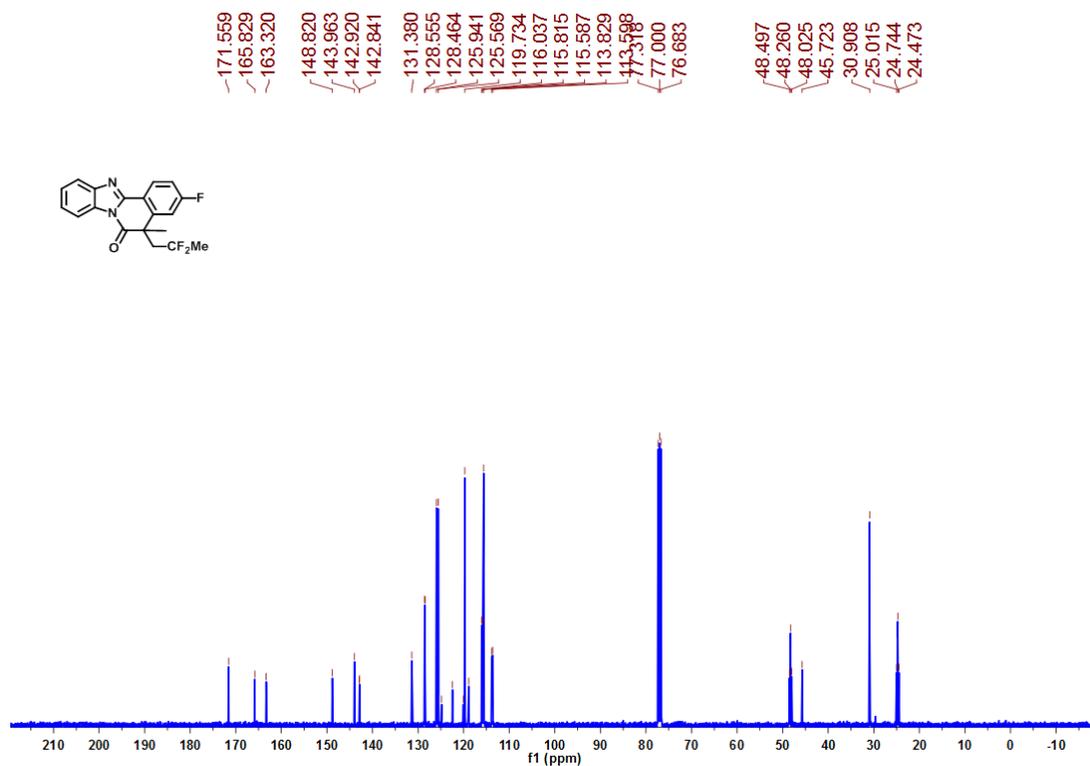
3b-¹⁹F NMR (471 MHz, CDCl₃)



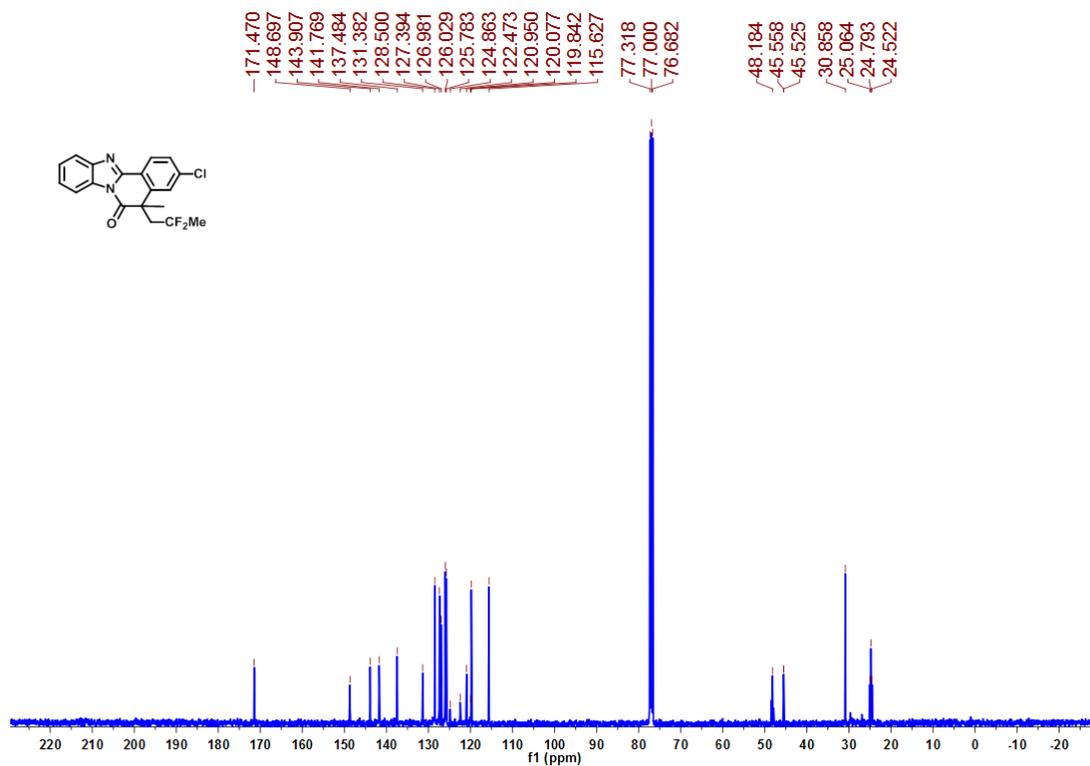
3c-¹H NMR (400 MHz, CDCl₃)



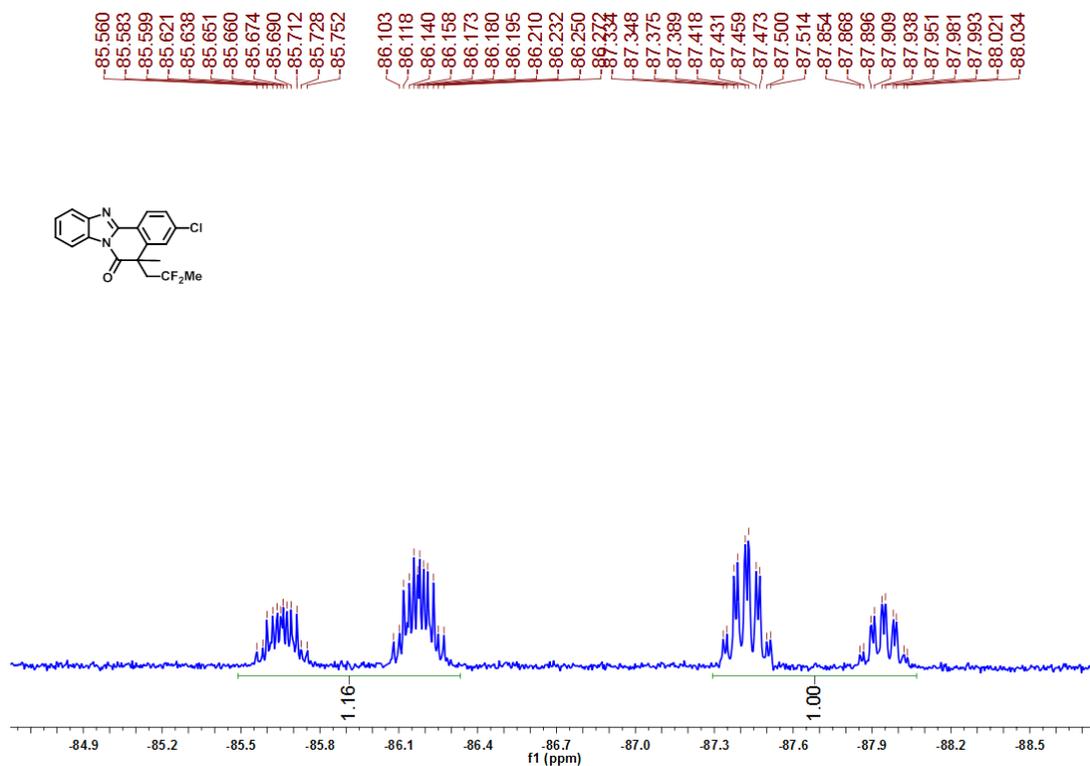
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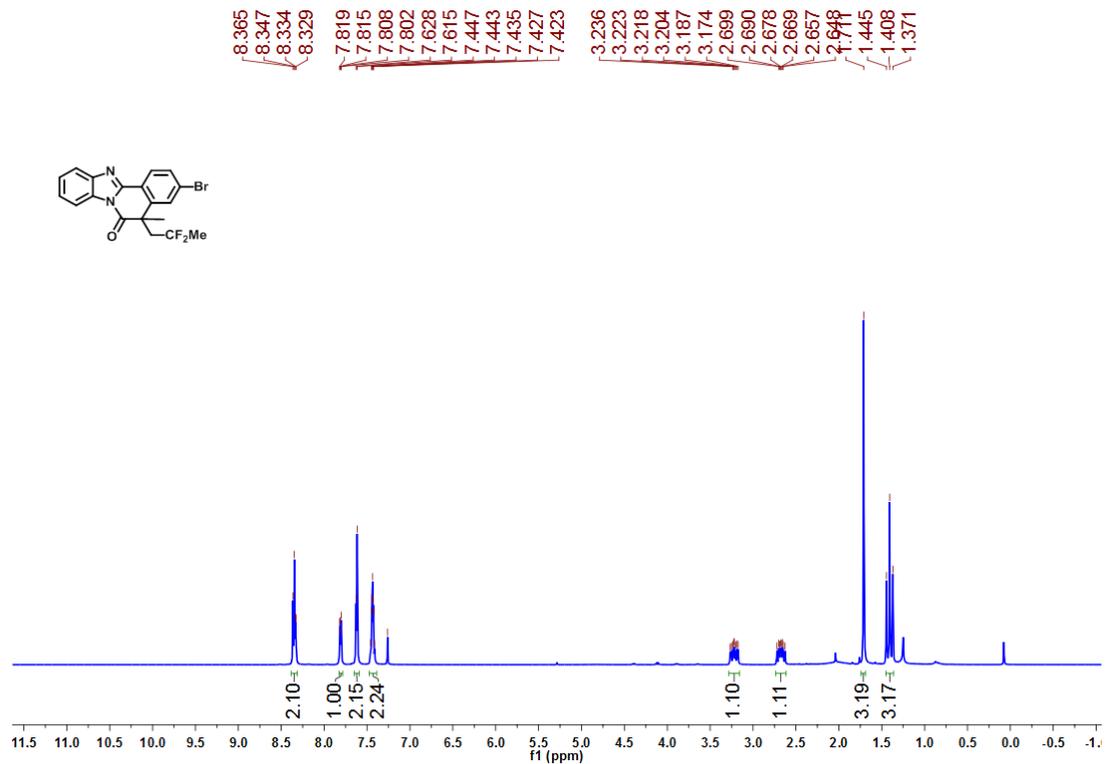
3d-¹³C{¹H} NMR (100 MHz, CDCl₃)



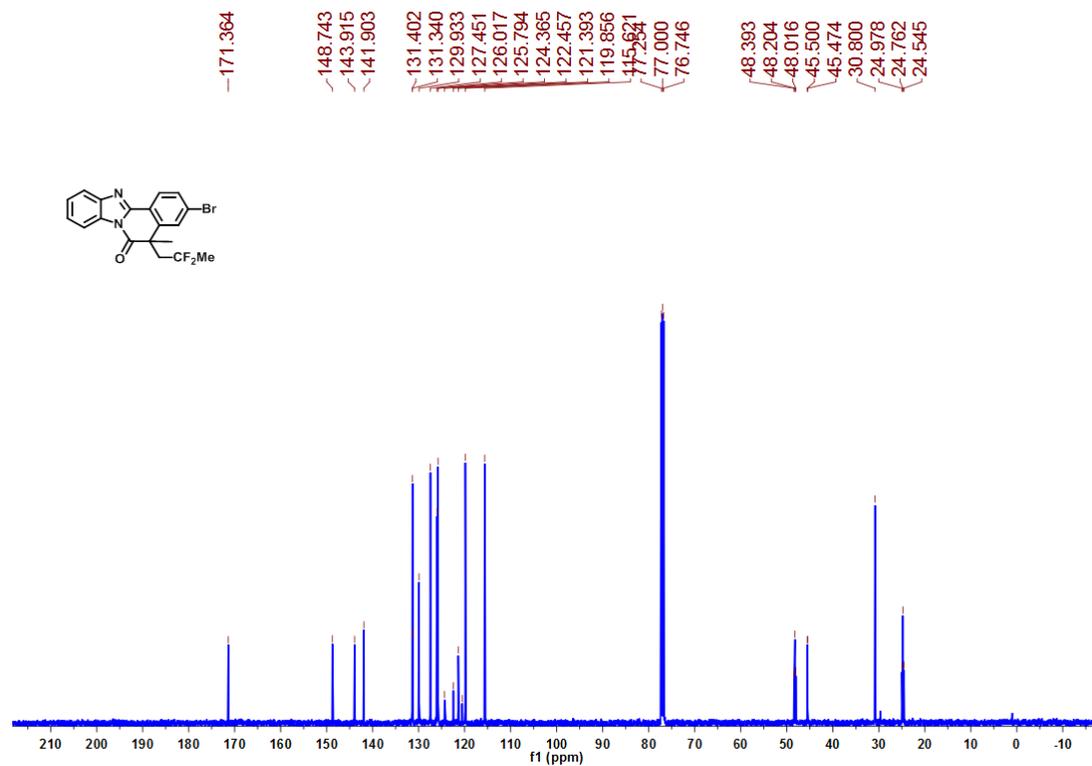
3d-¹⁹F NMR (471 MHz, CDCl₃)



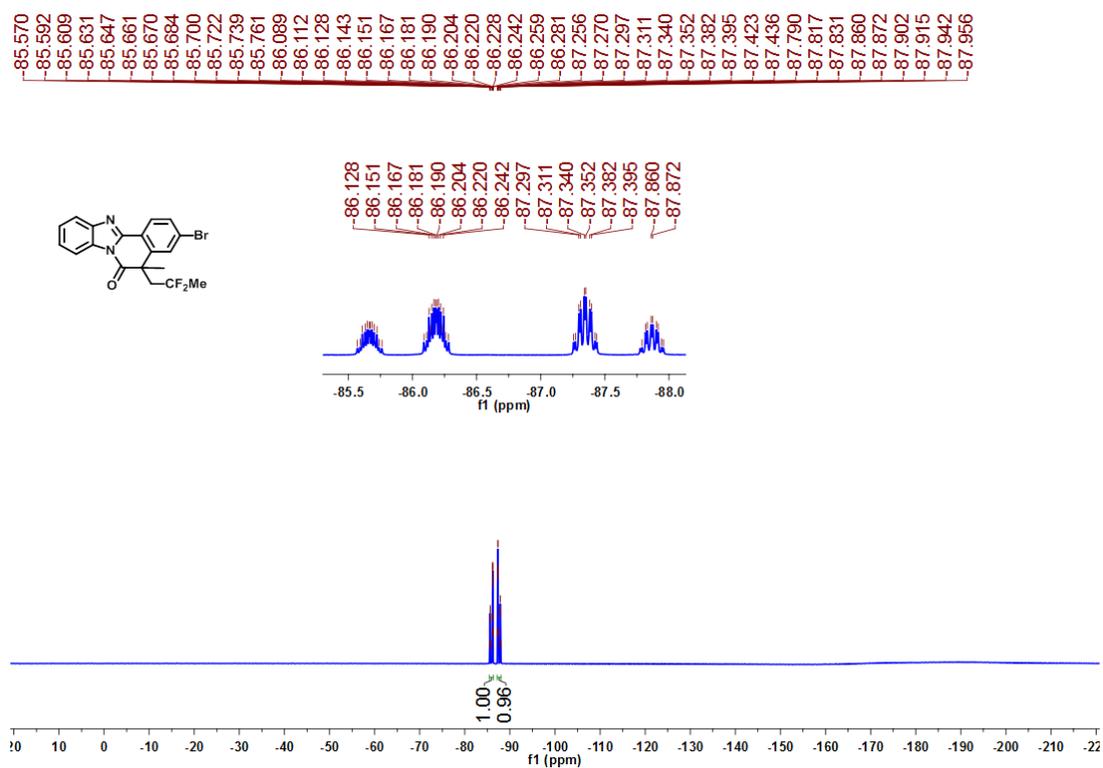
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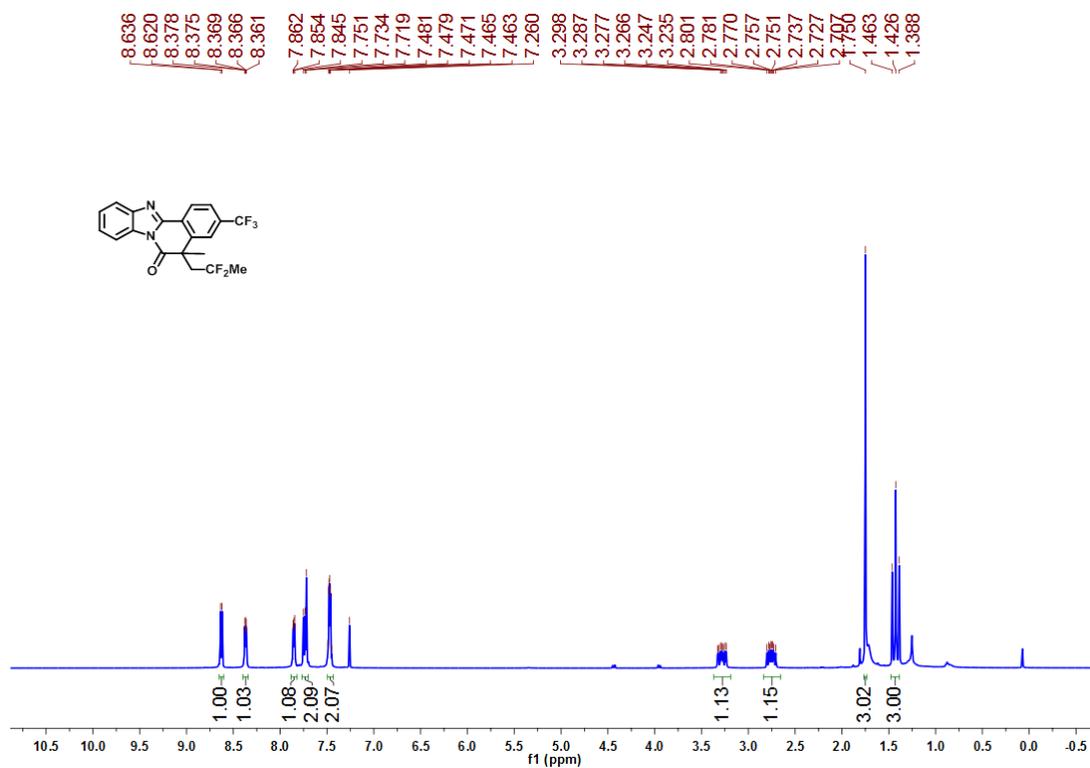
3e-¹³C{¹H} NMR (125 MHz, CDCl₃)



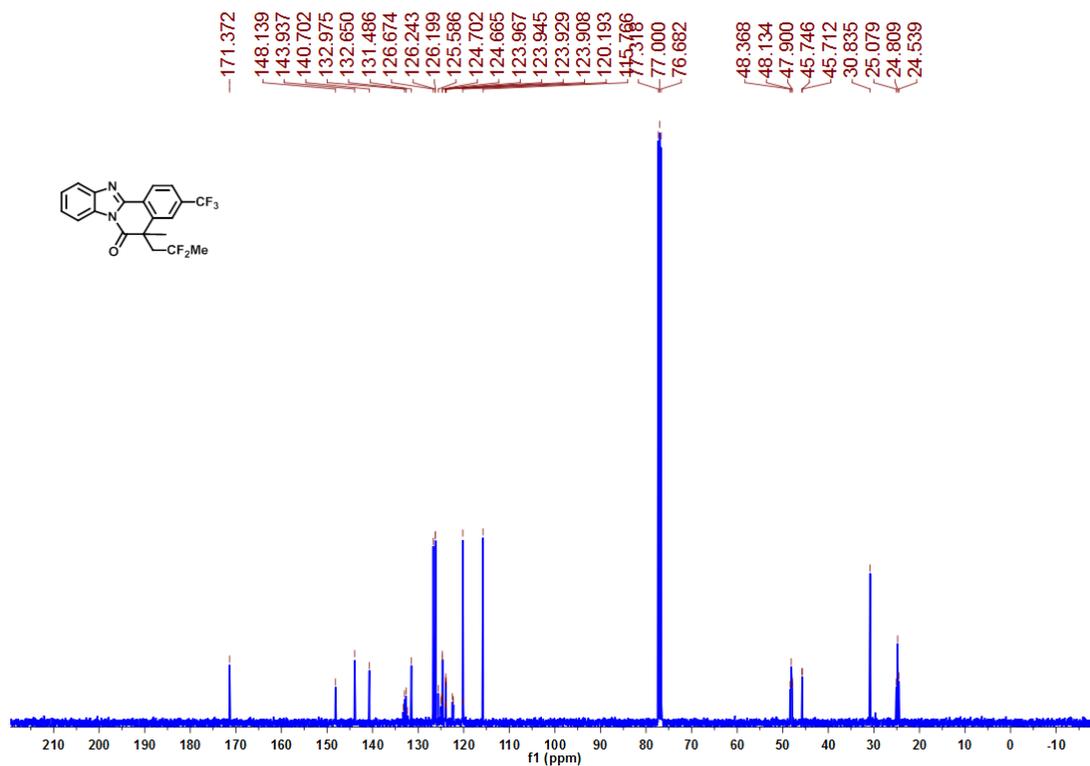
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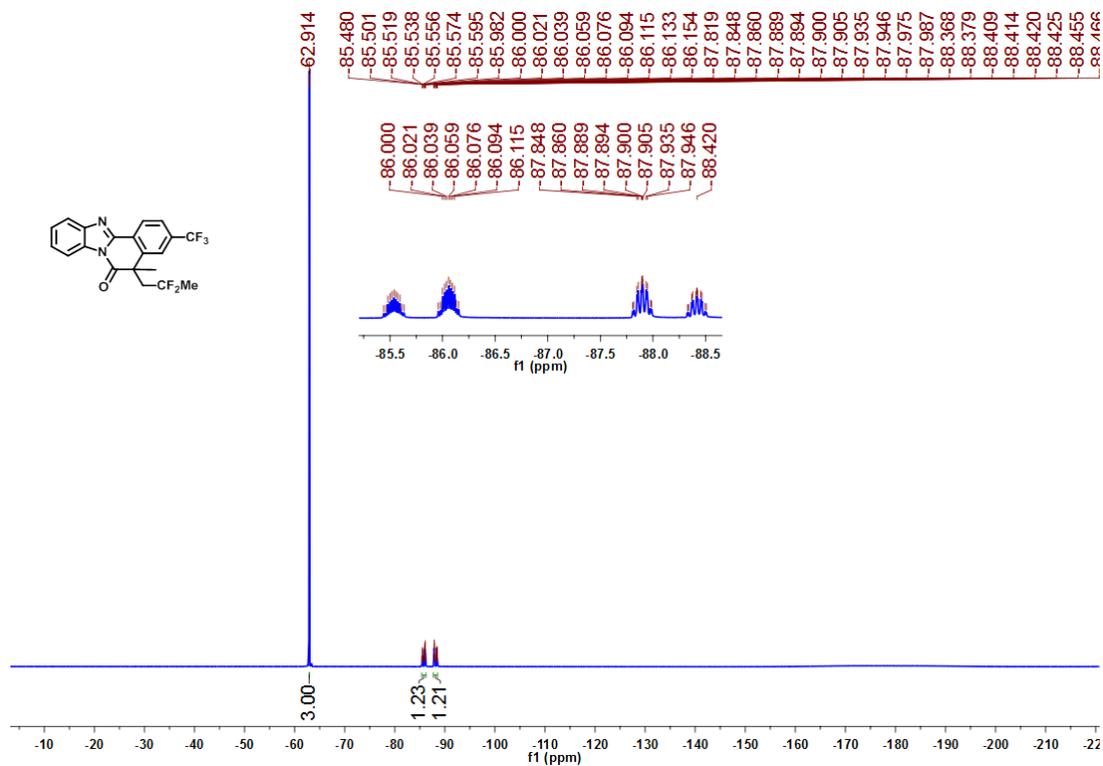
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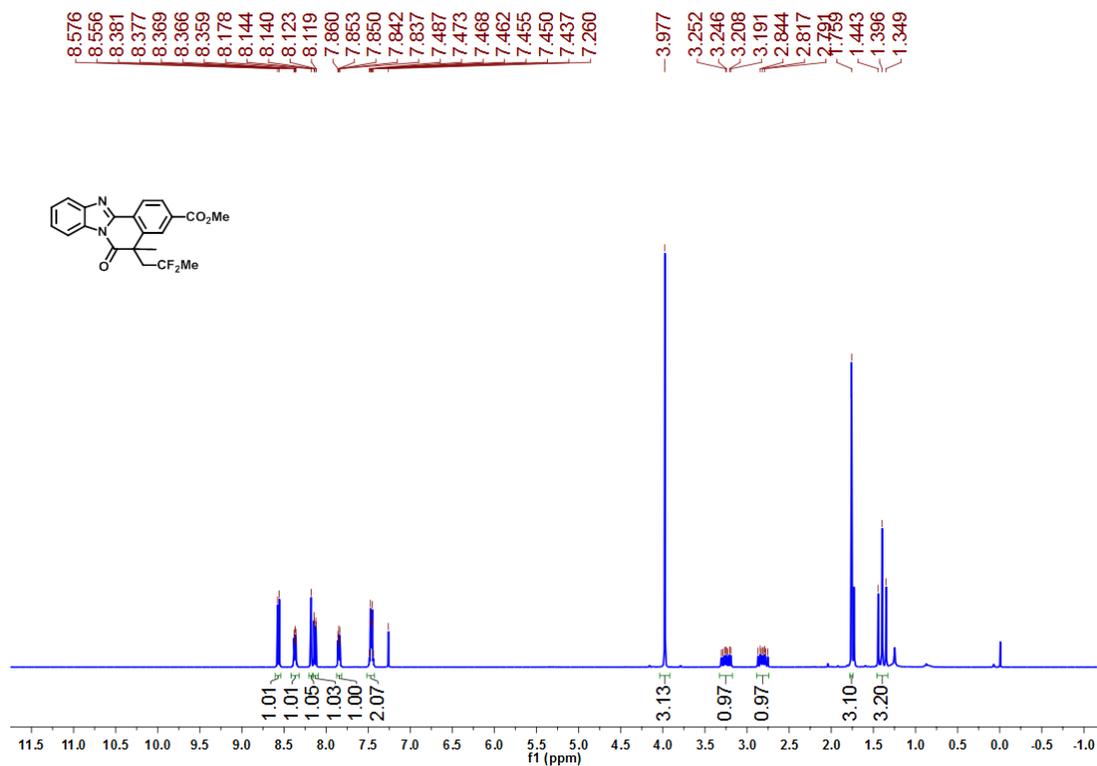
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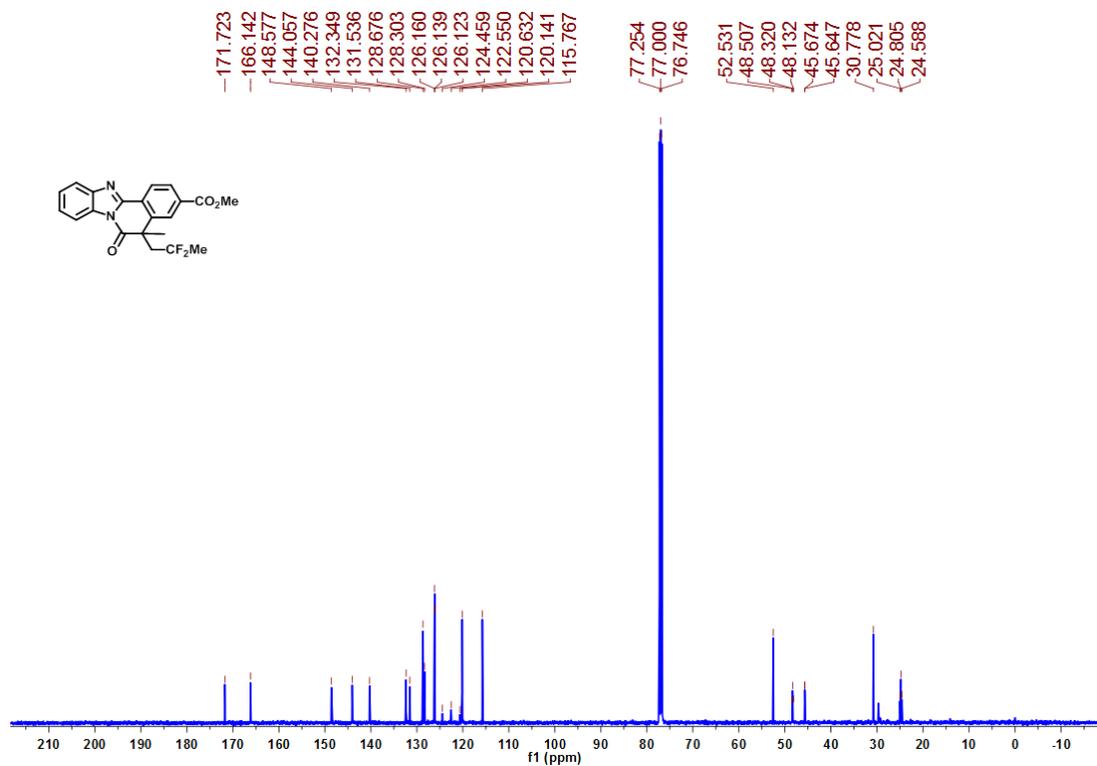
3f- ^{19}F NMR (471 MHz, CDCl_3)



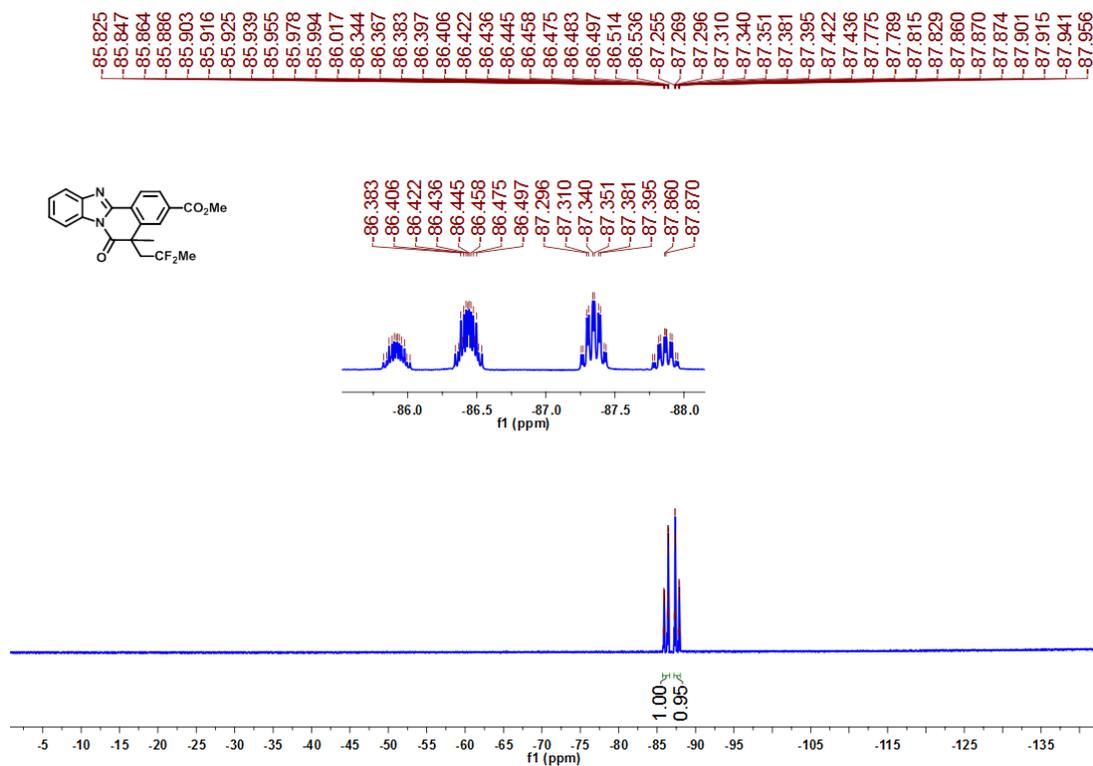
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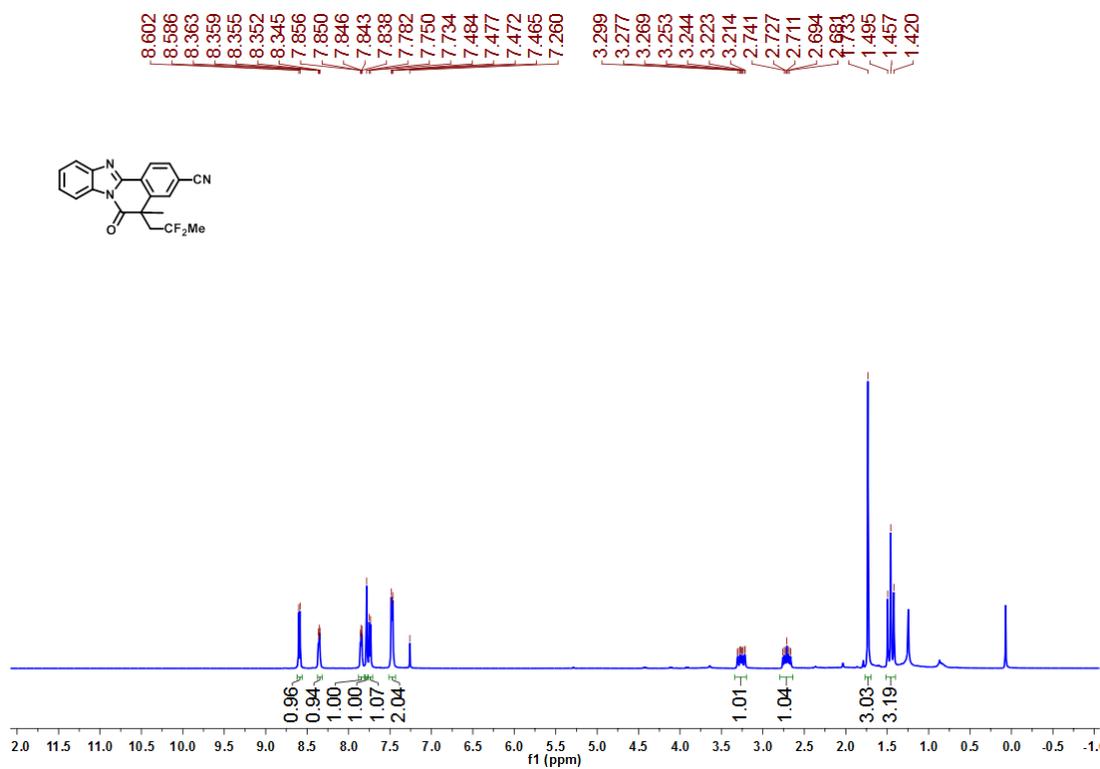
¹³C{¹H} NMR (125 MHz, CDCl₃)



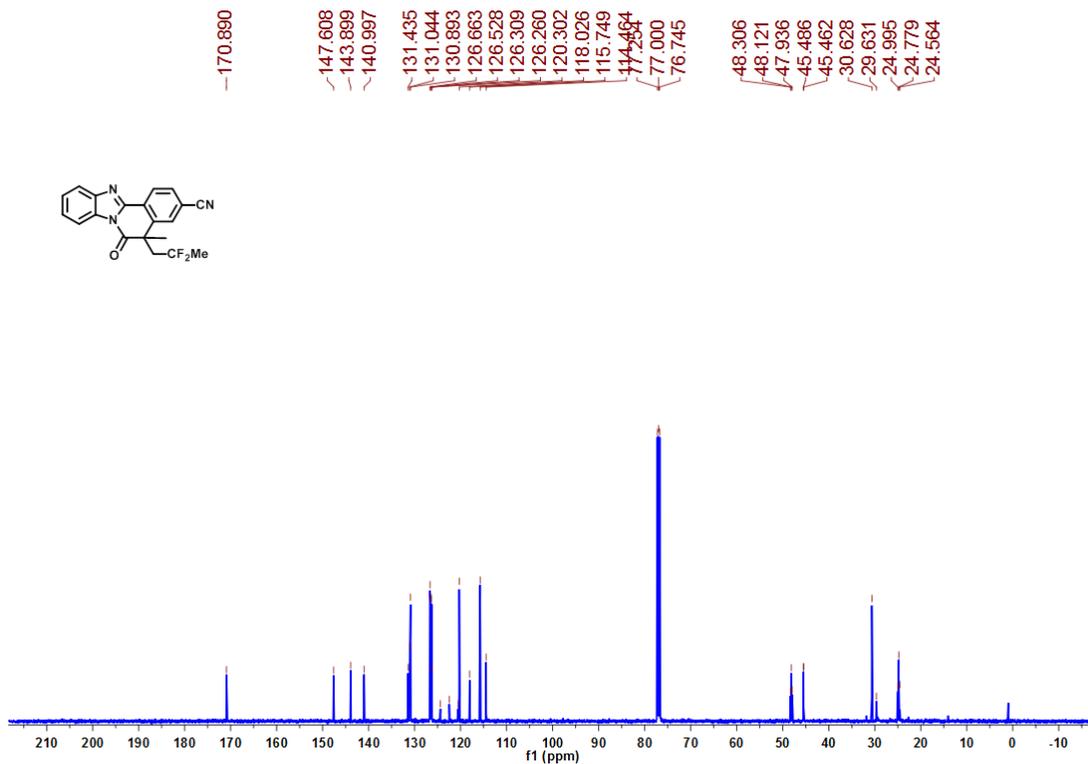
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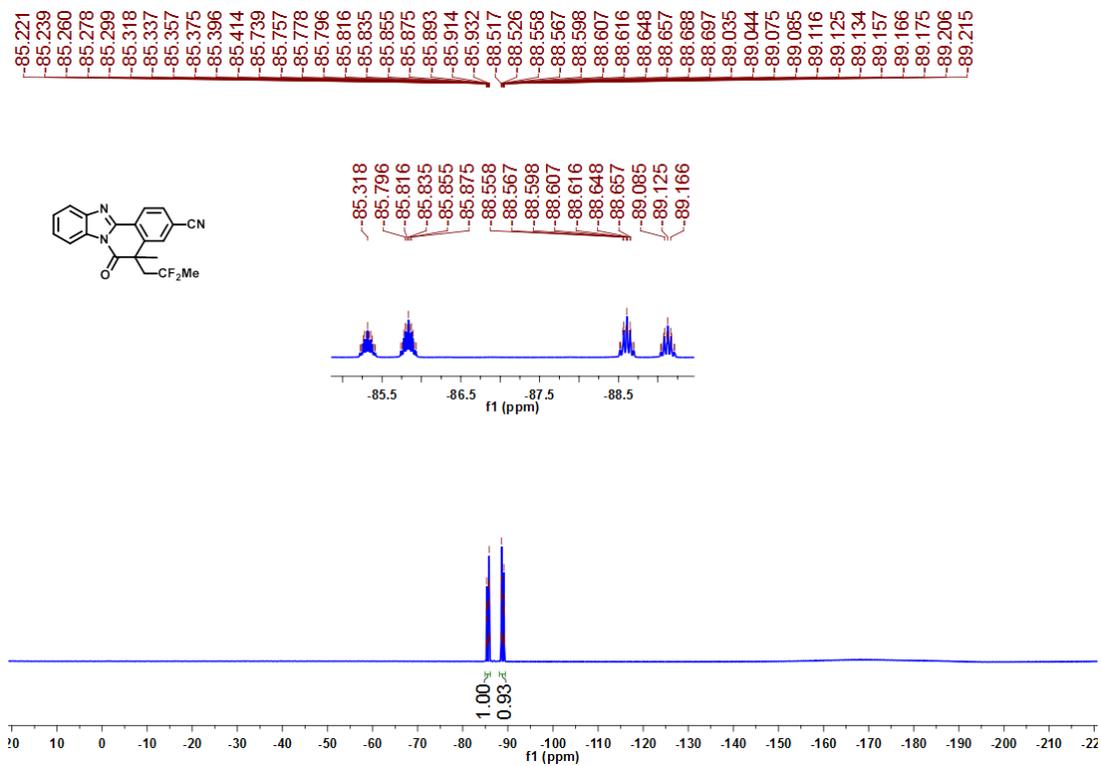
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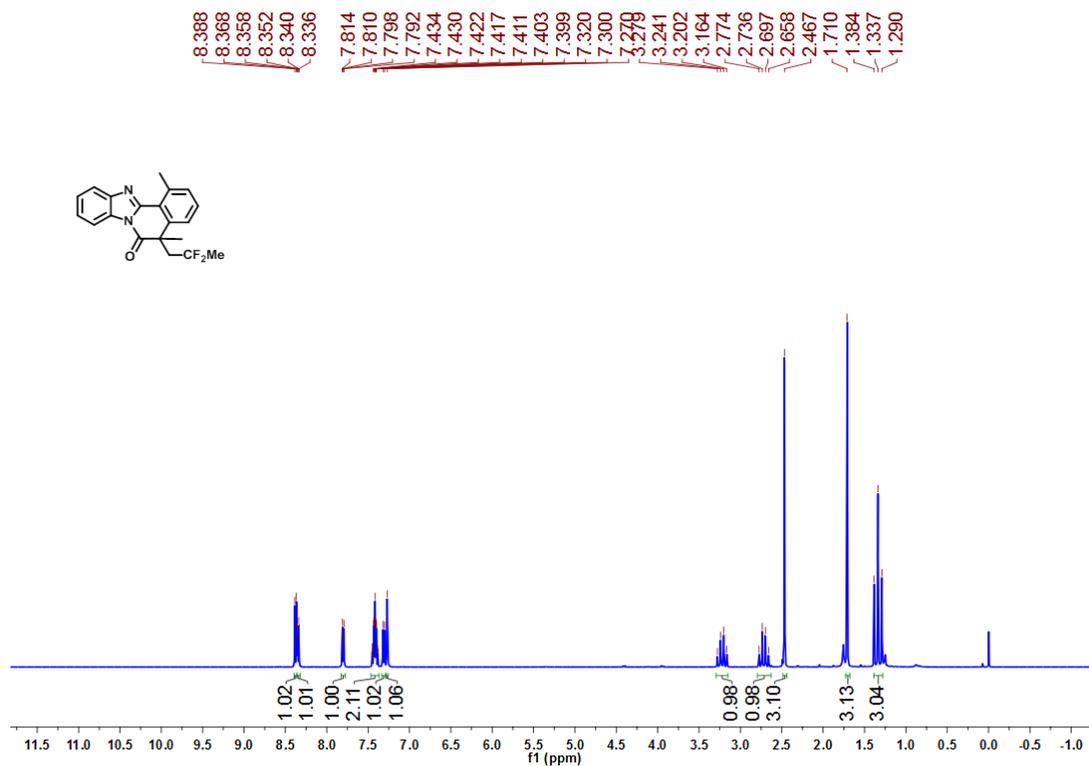
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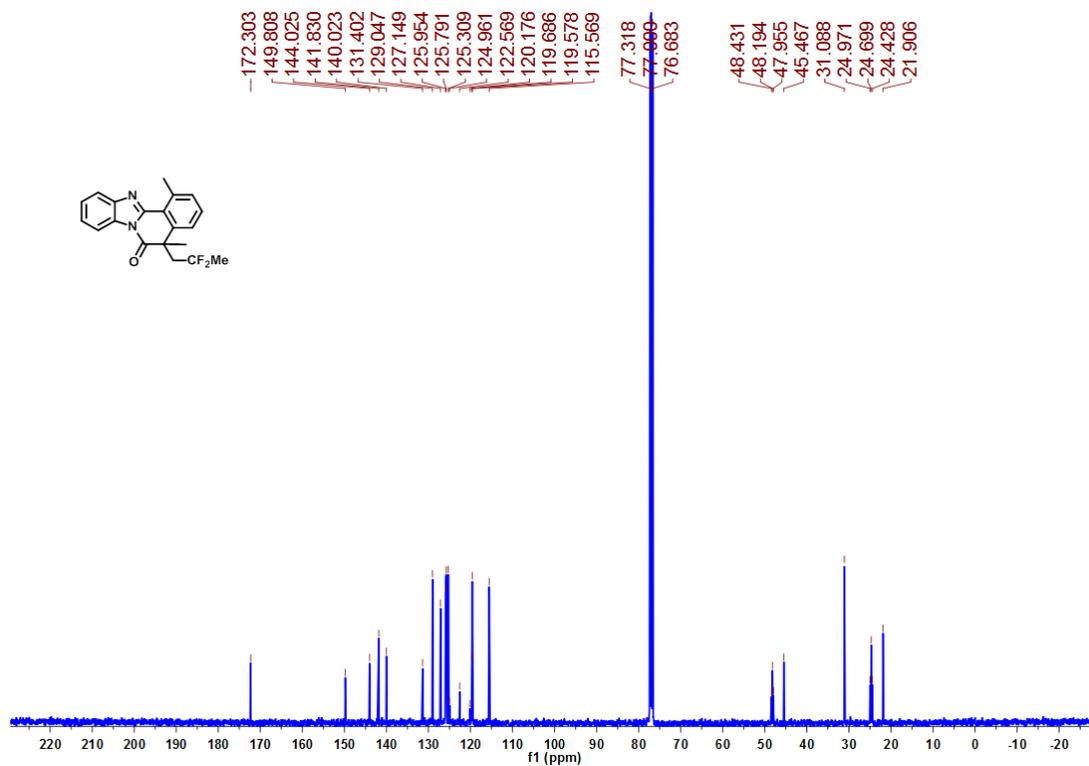
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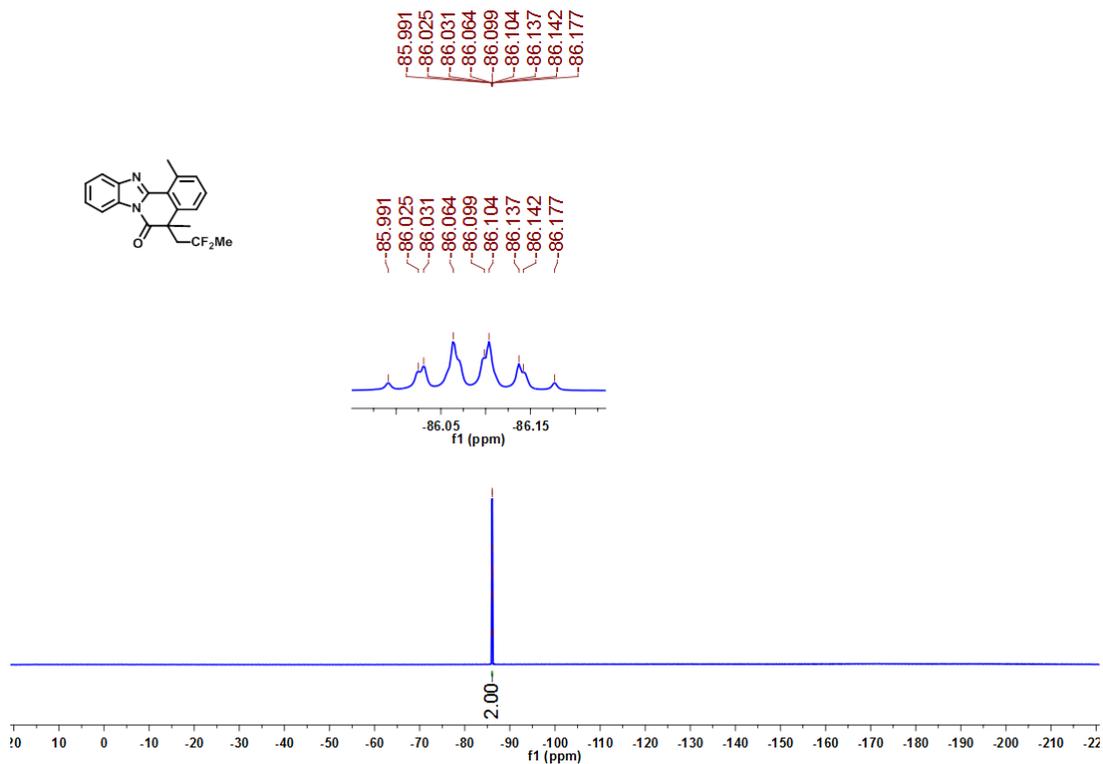
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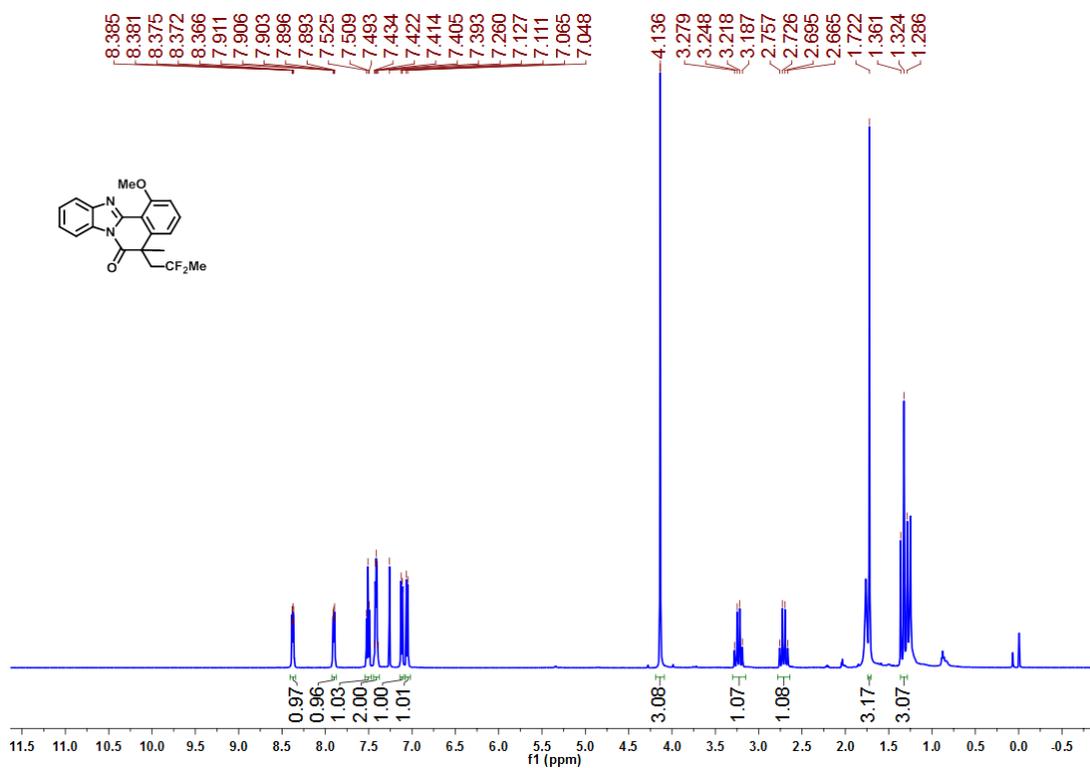
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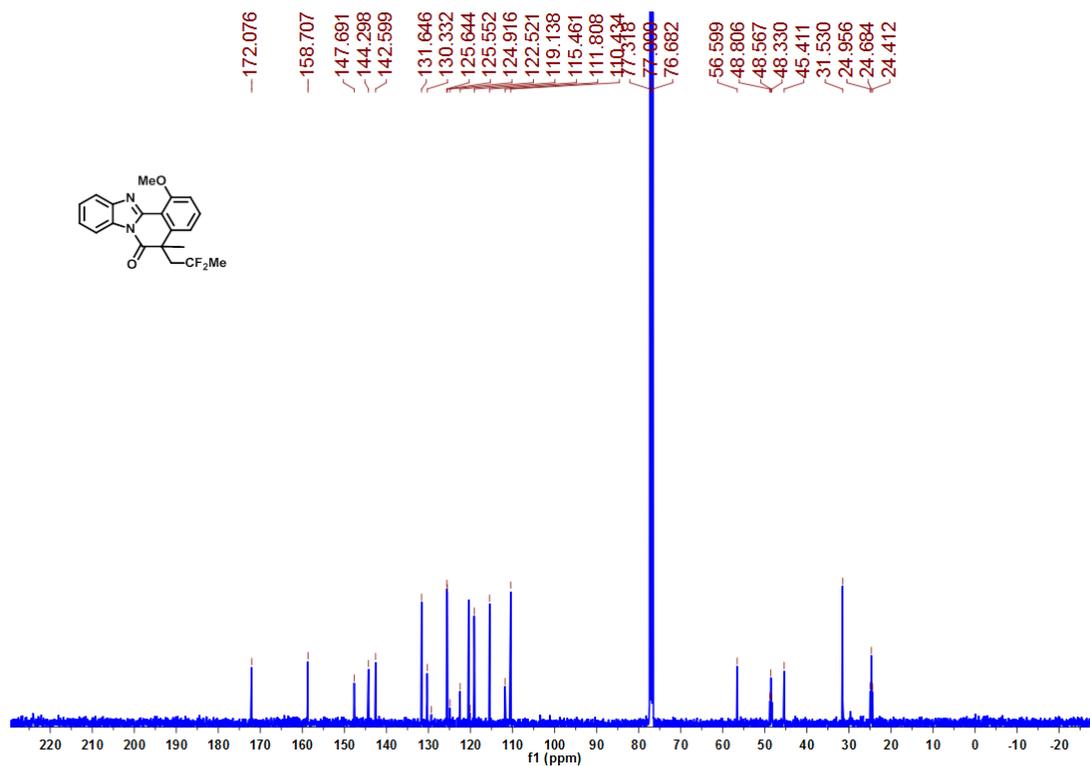
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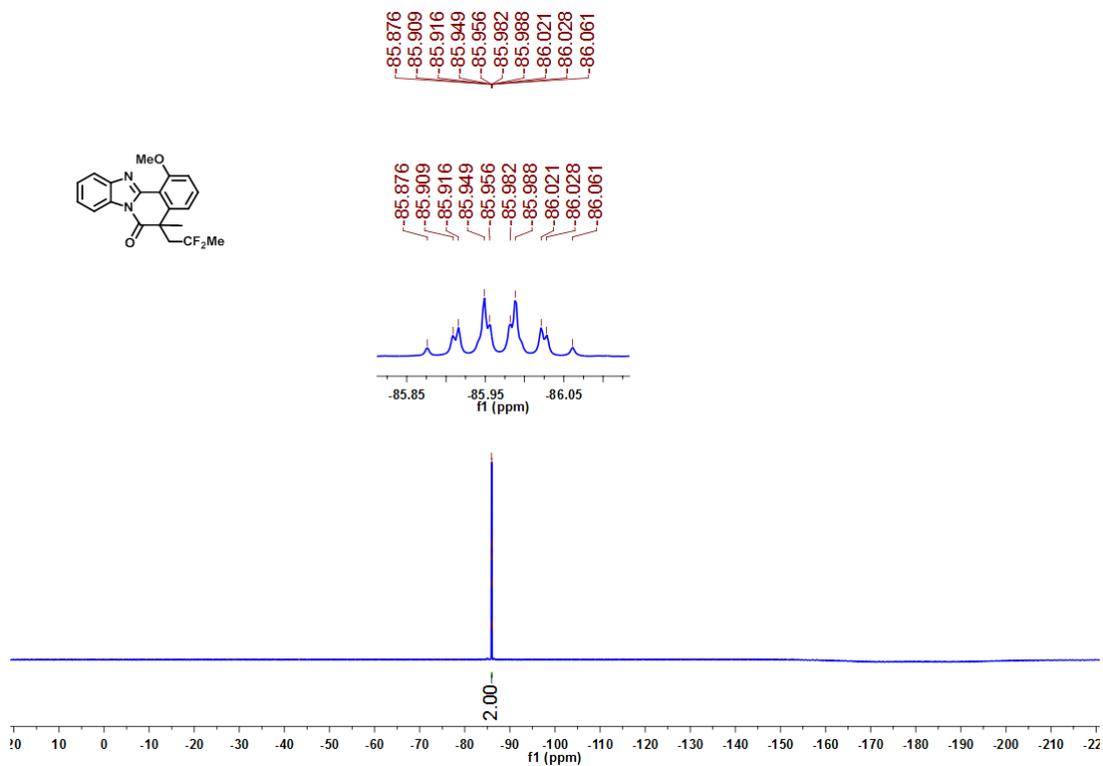
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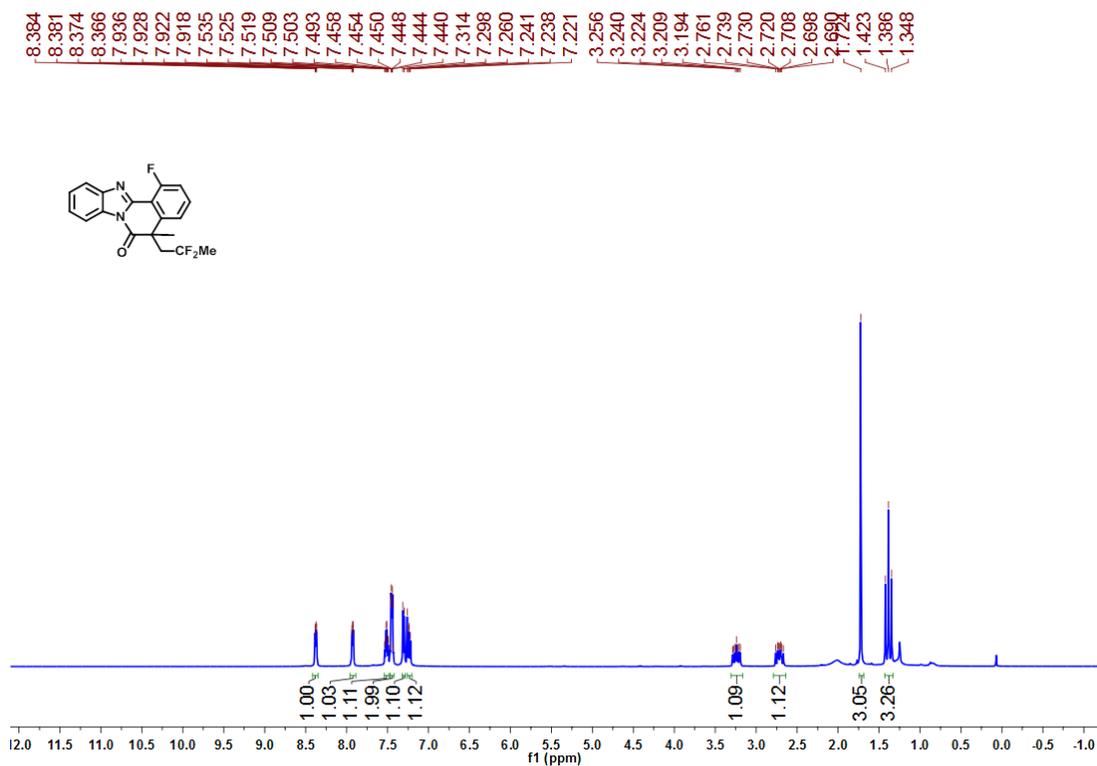
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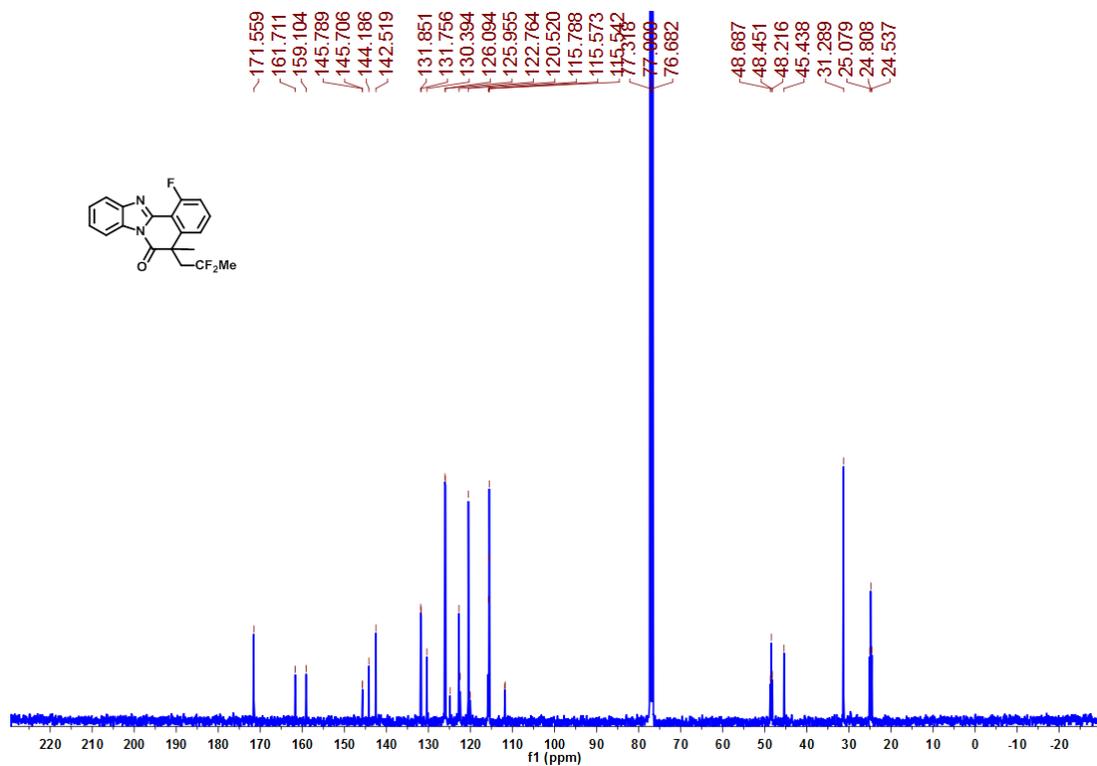
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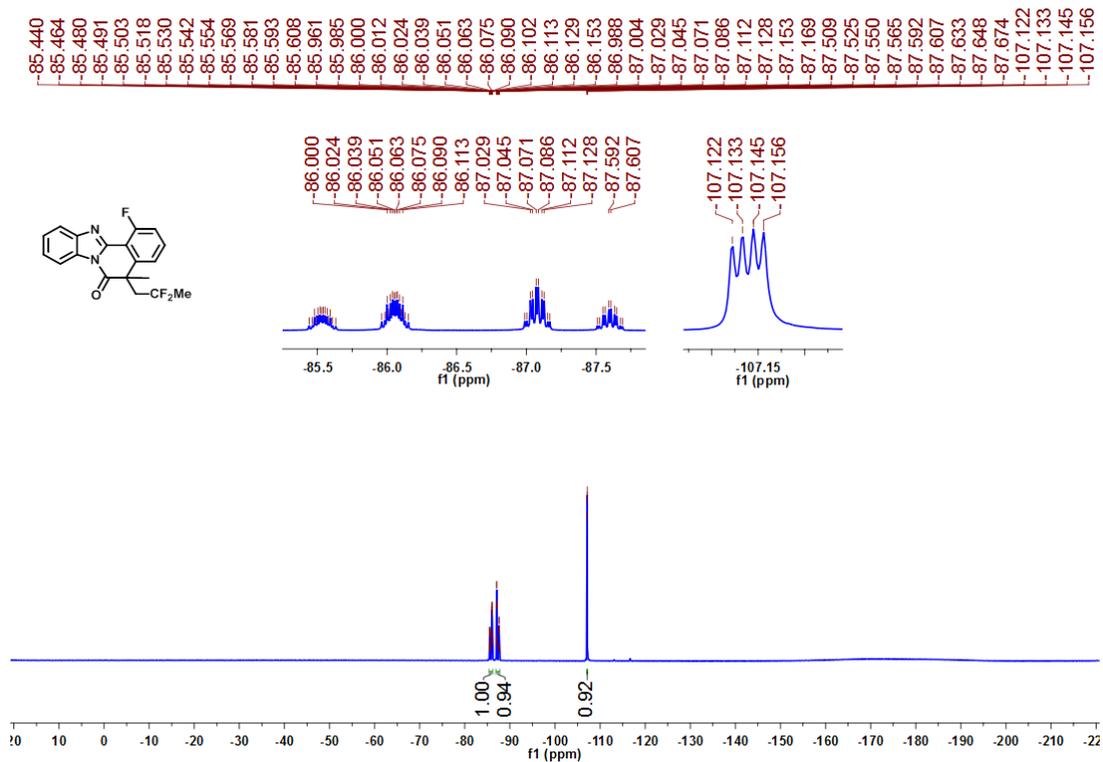
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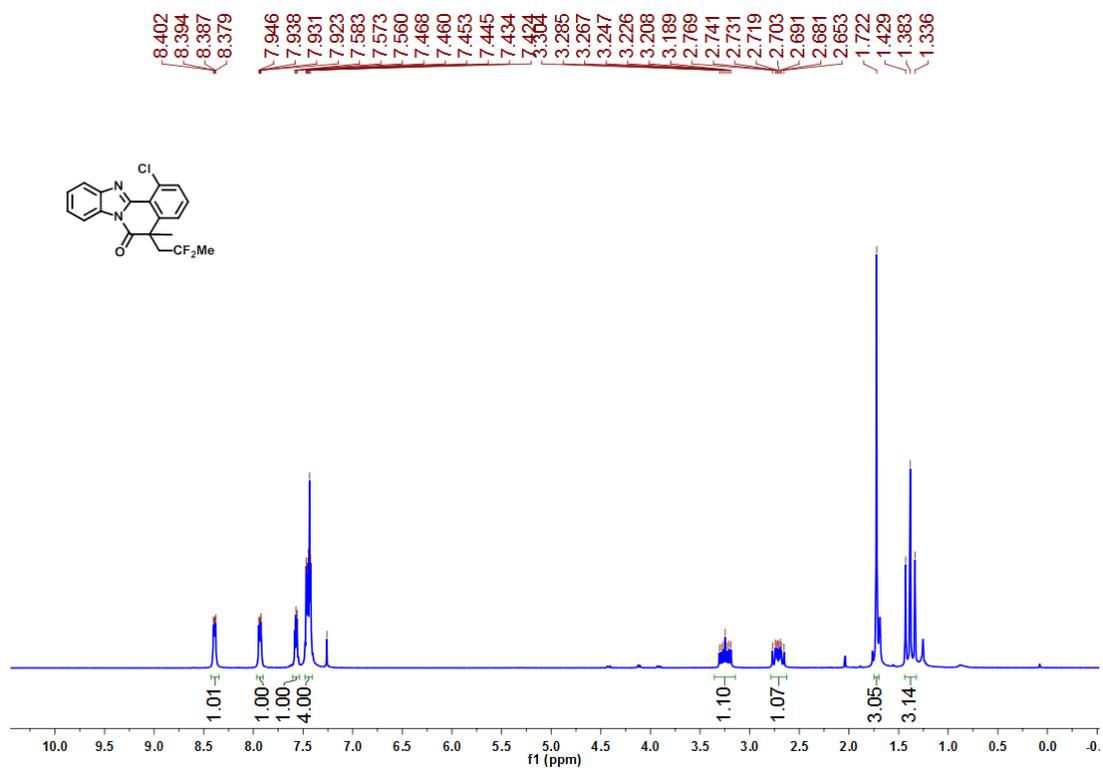
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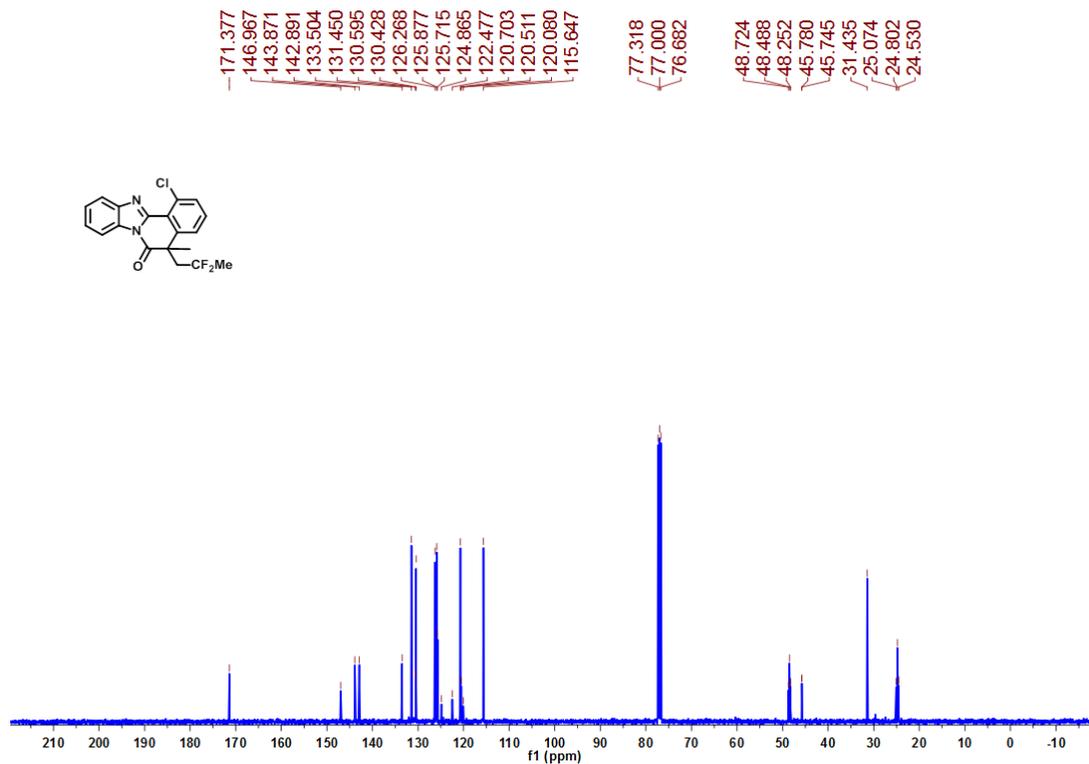
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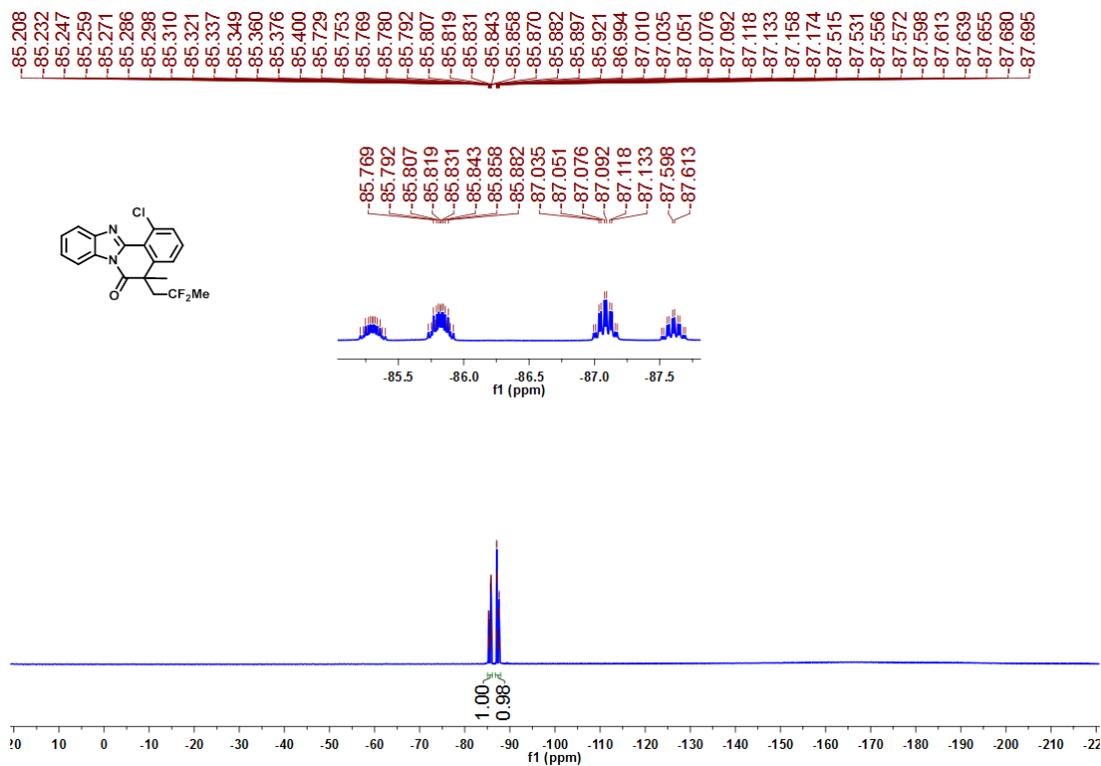
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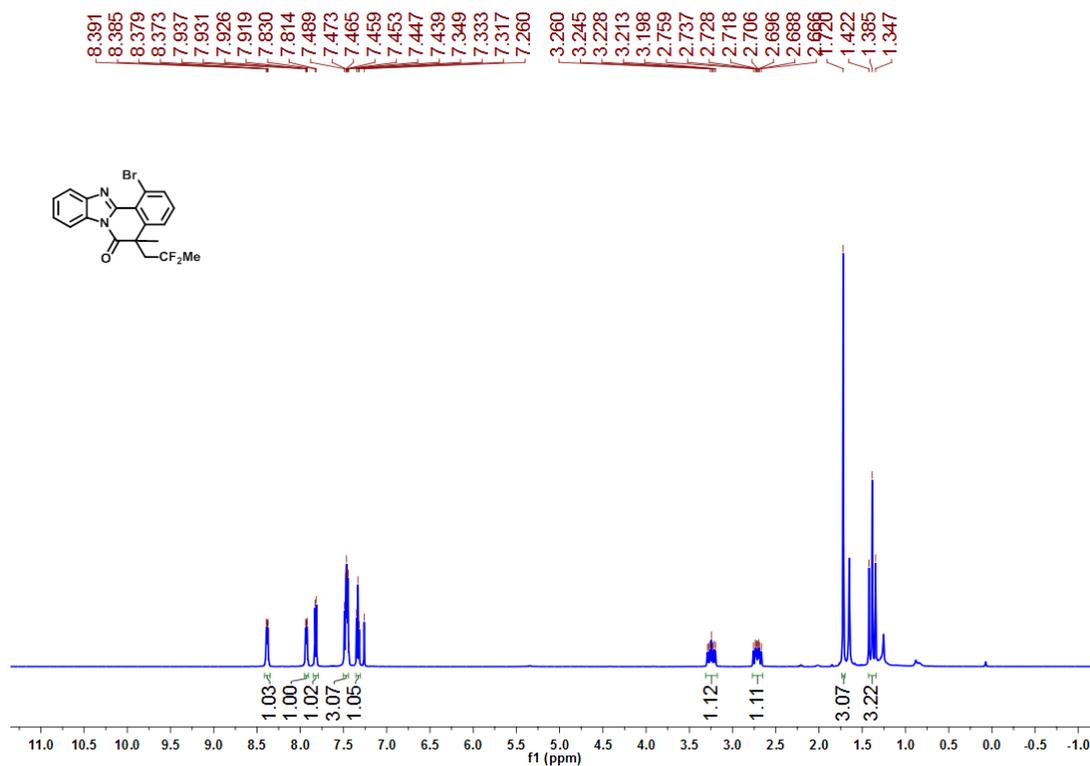
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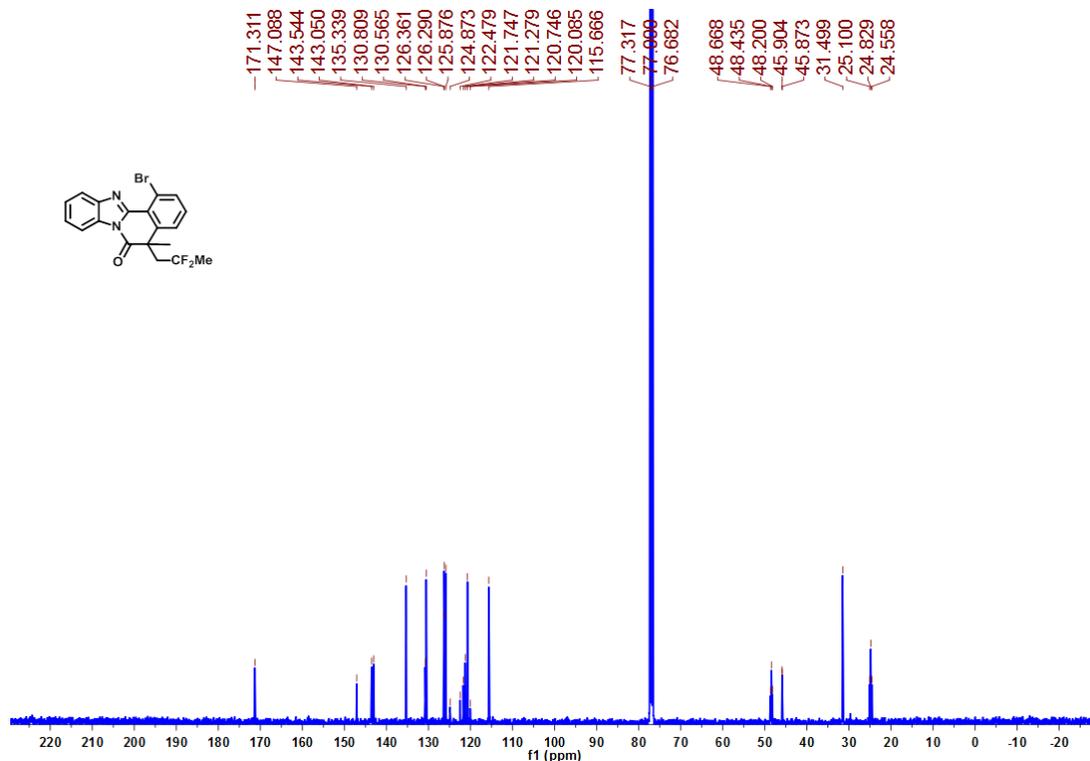
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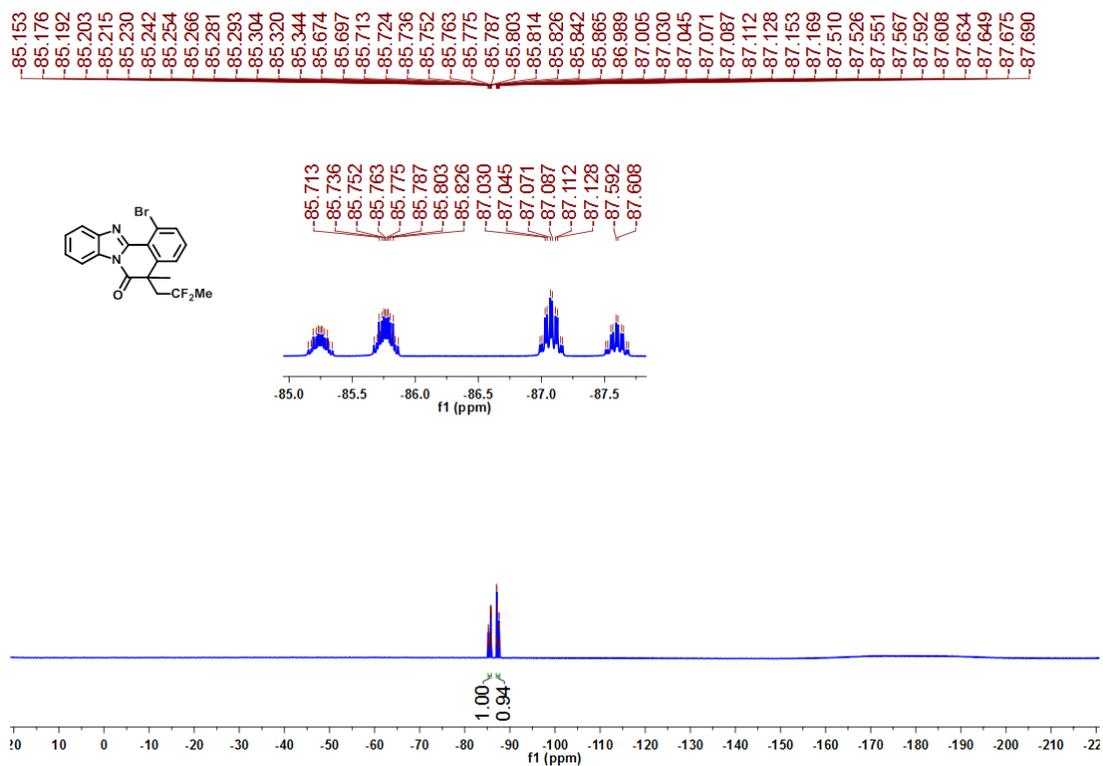
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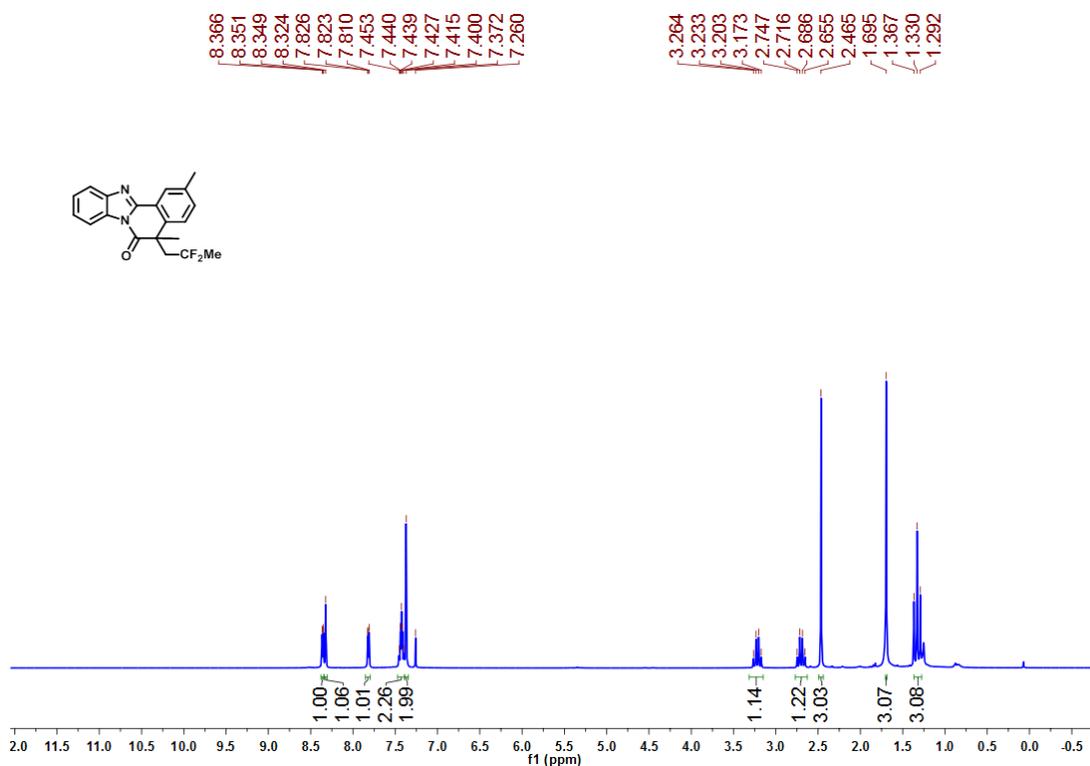
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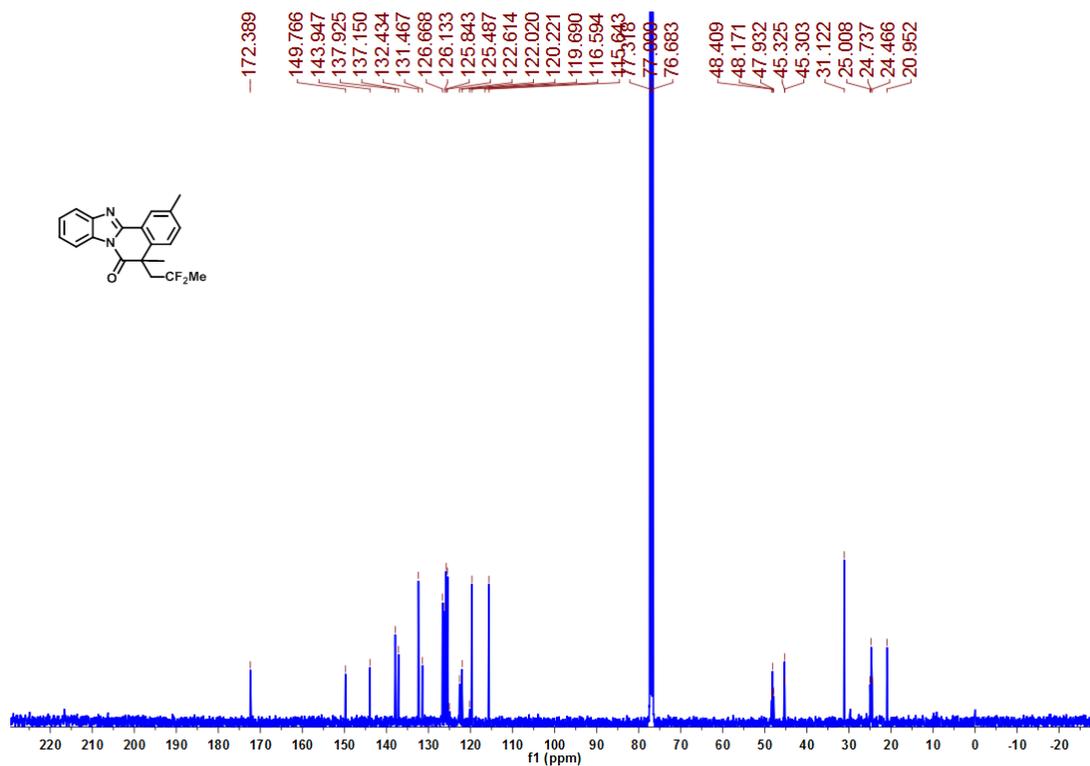
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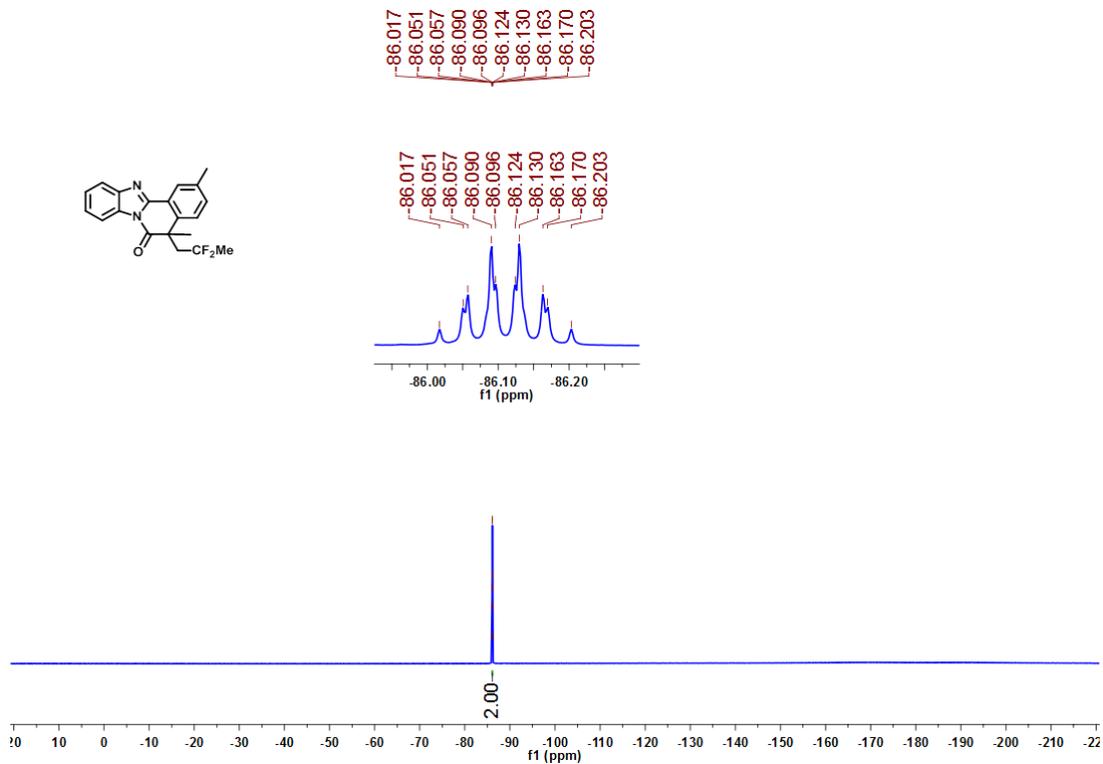
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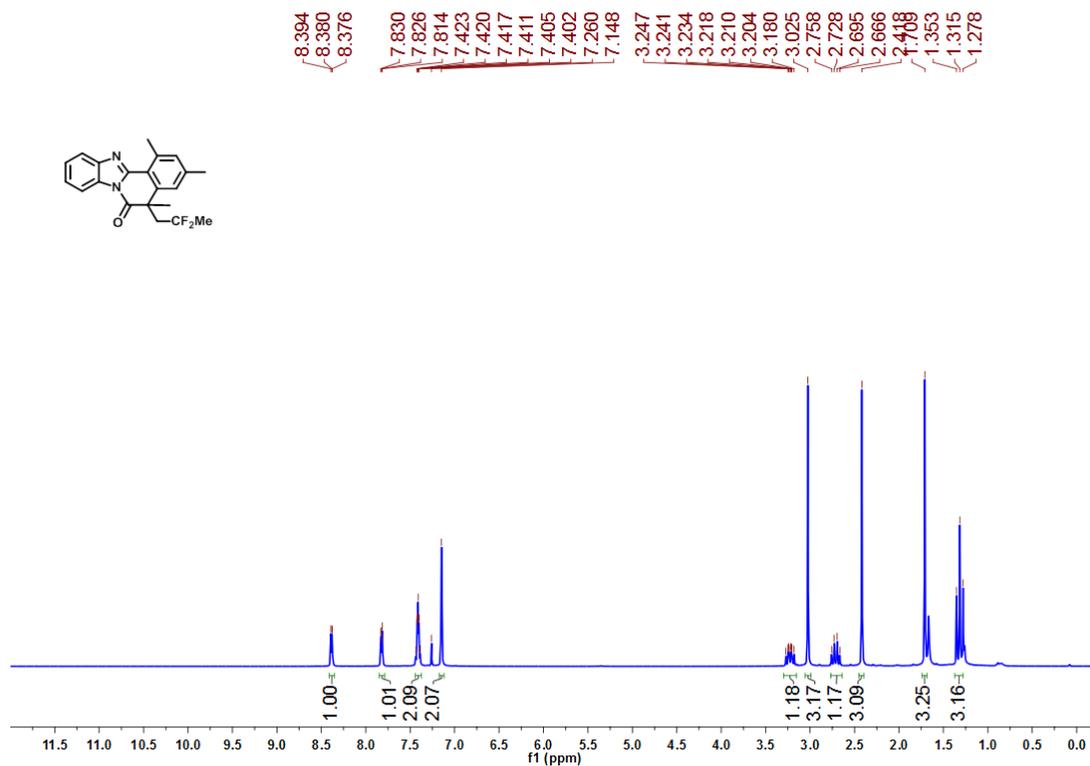
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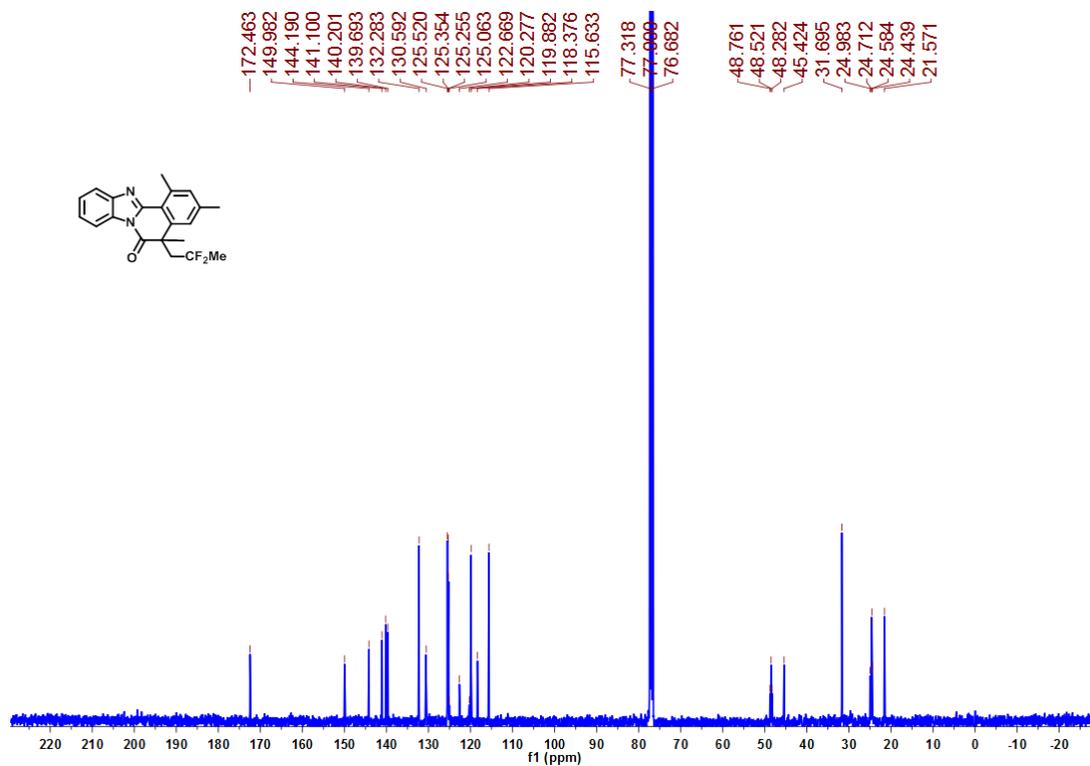
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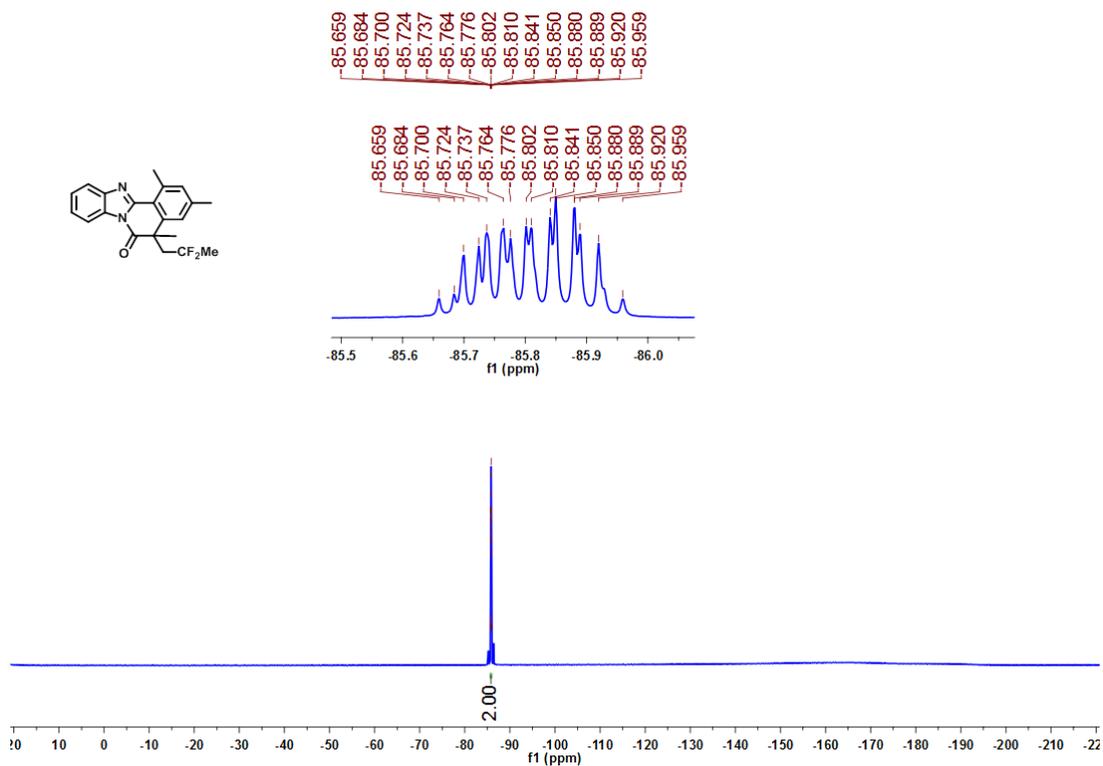
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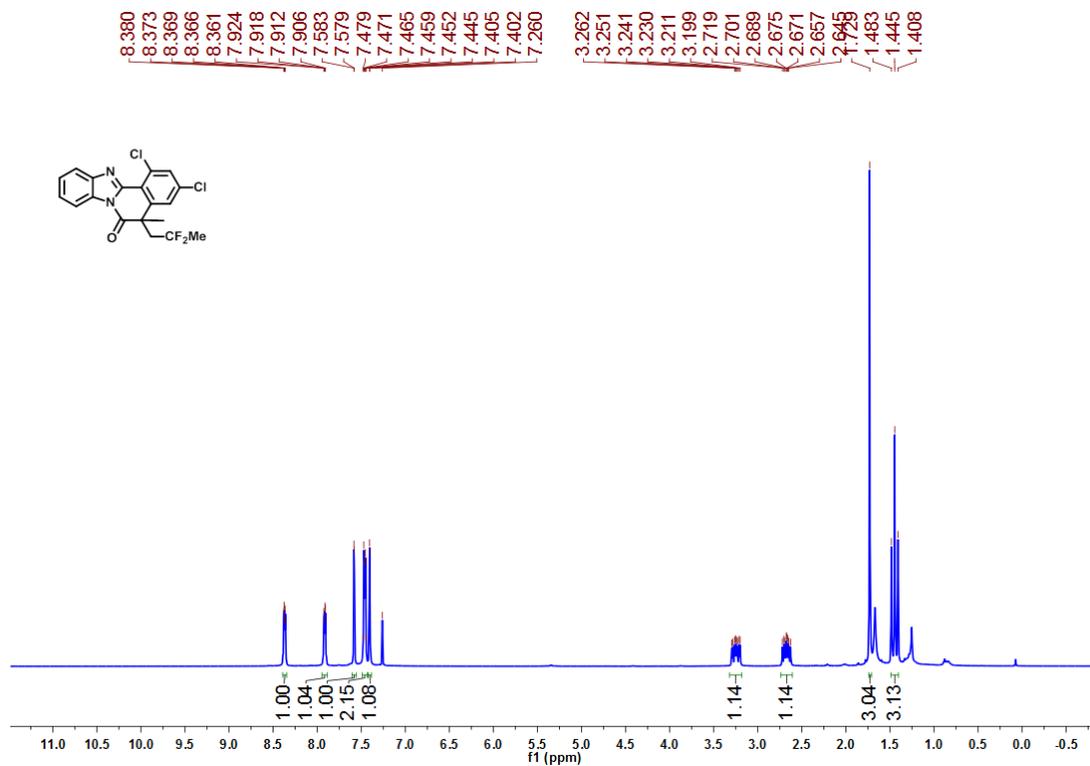
30-¹³C{¹H} NMR (100 MHz, CDCl₃)



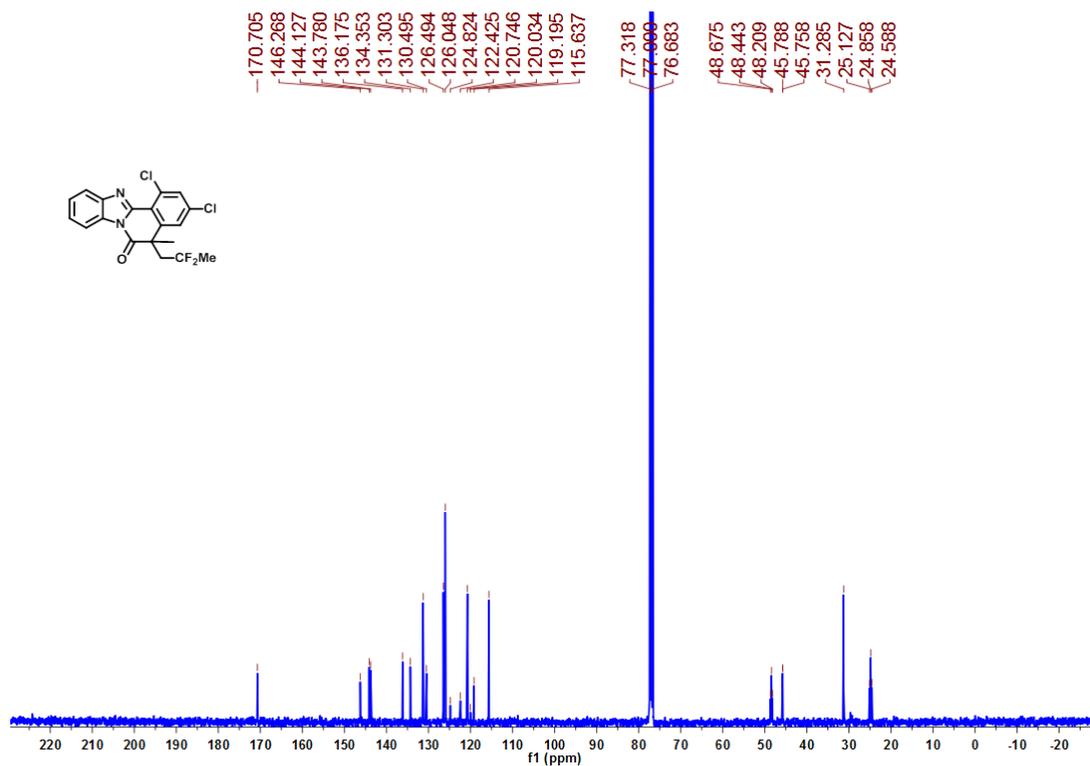
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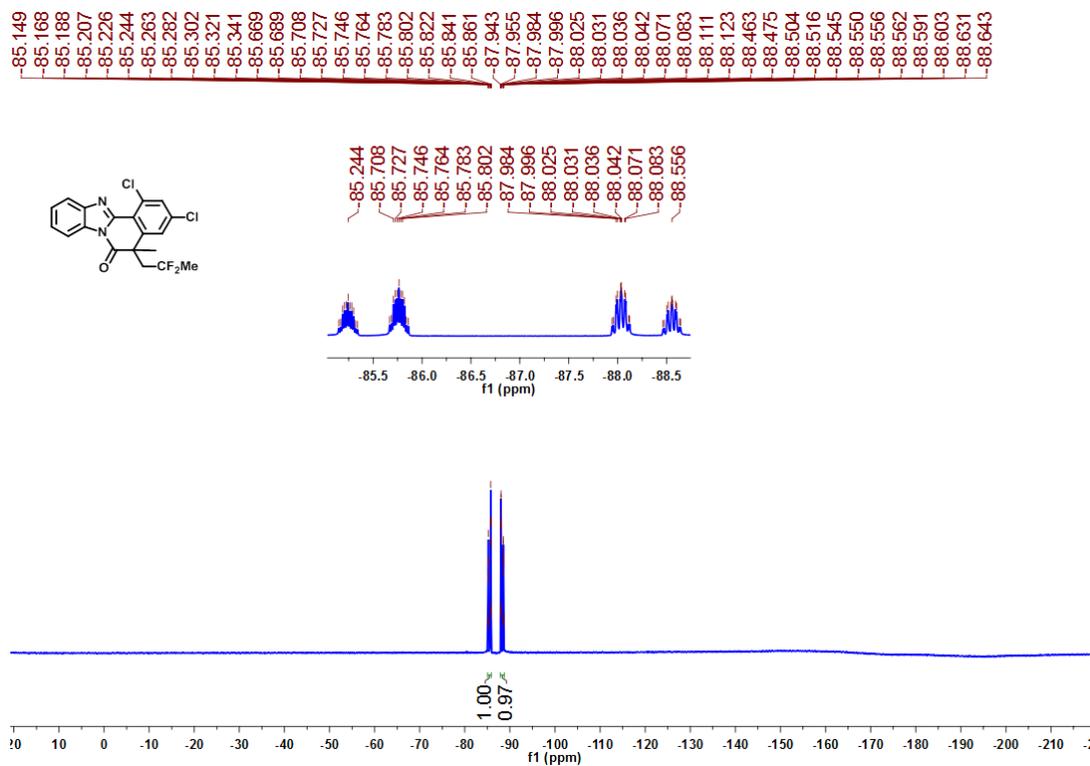
3p- ^1H NMR (500 MHz, CDCl_3)



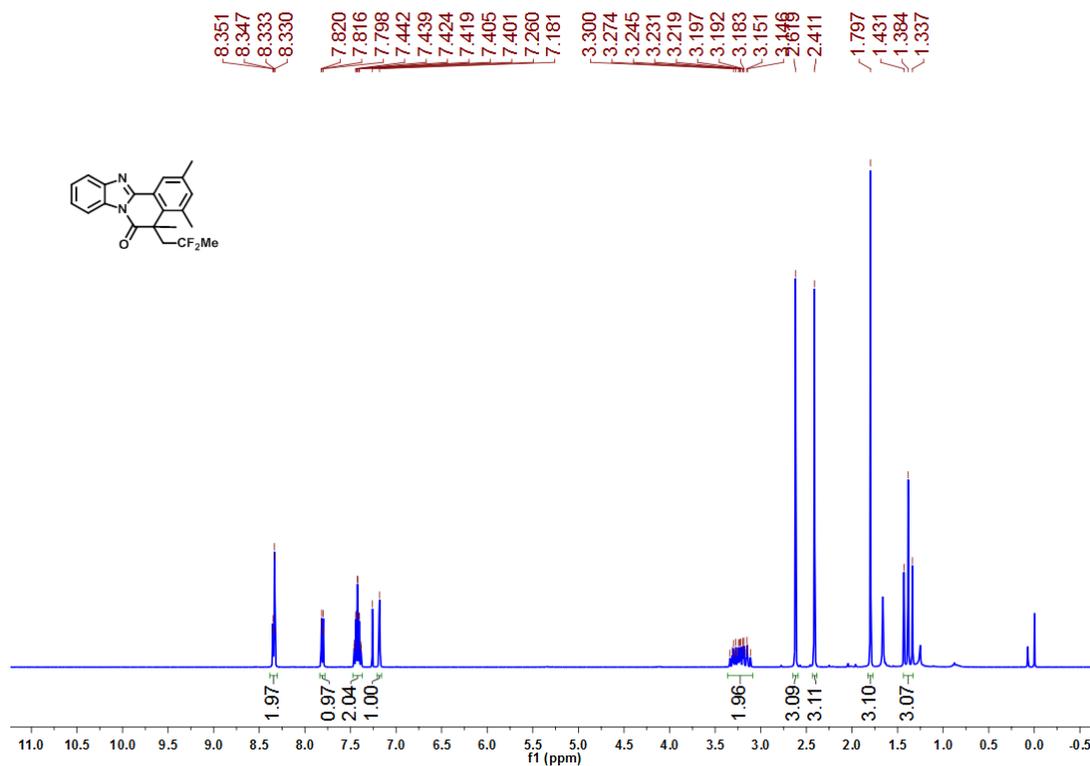
3p- $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3)



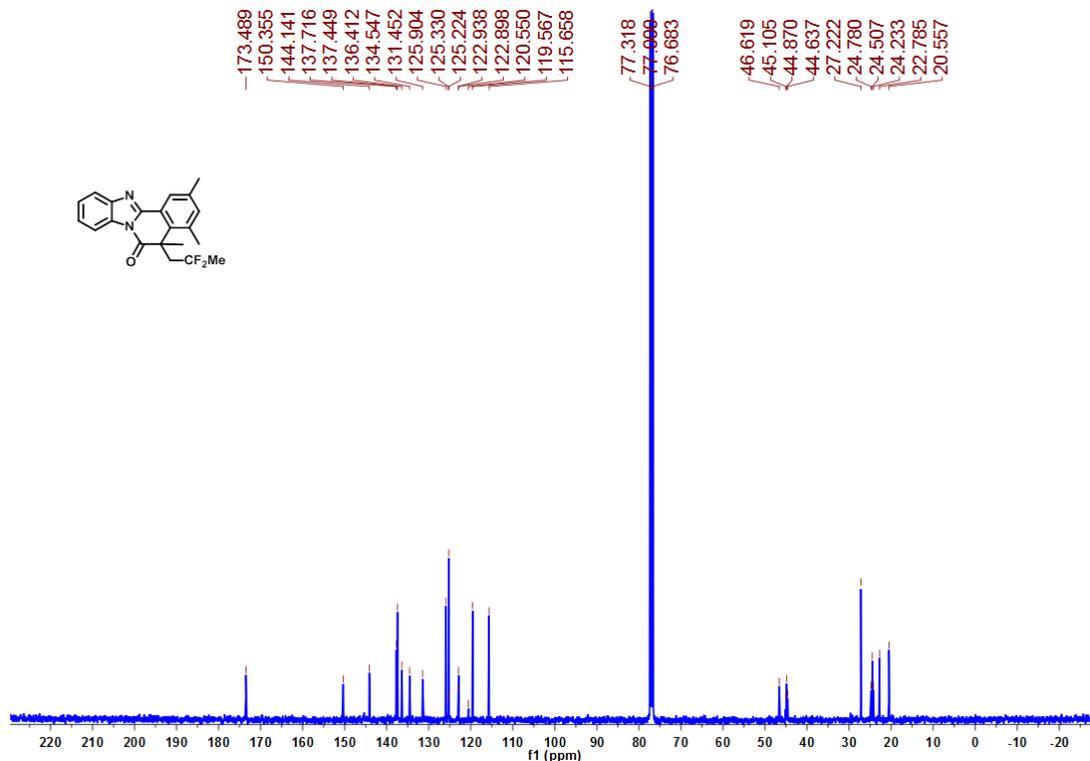
3p-¹⁹F NMR (471 MHz, CDCl₃)



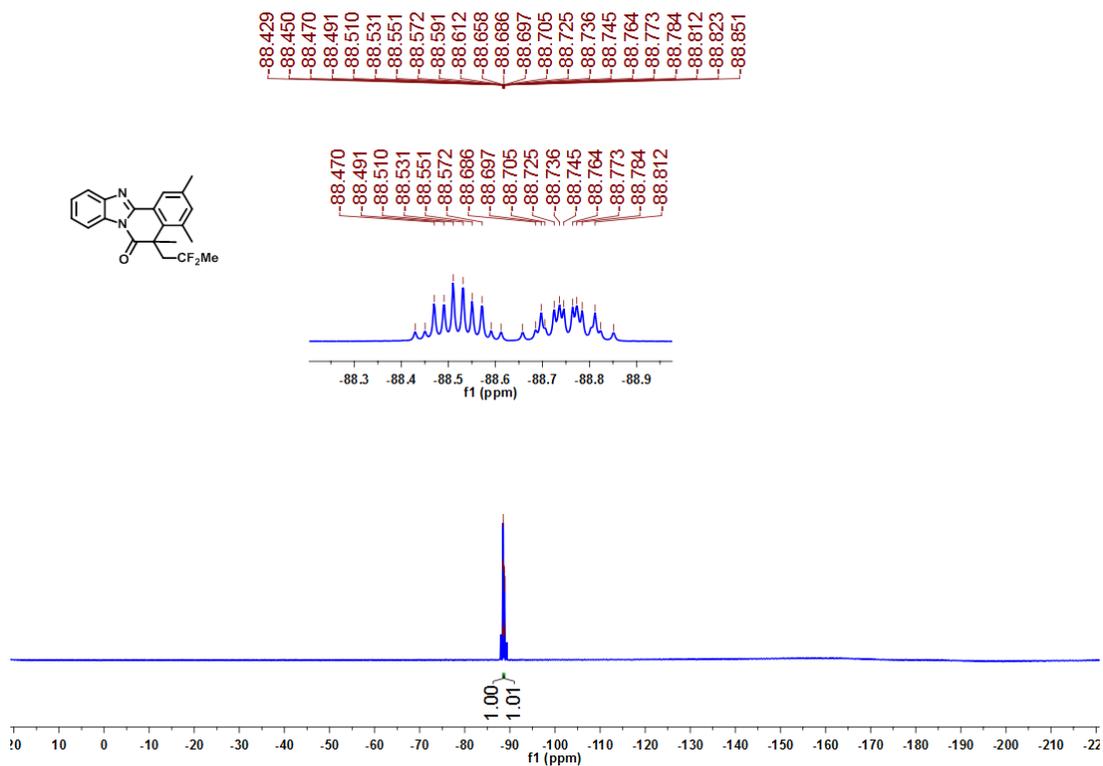
3q-¹H NMR (400 MHz, CDCl₃)



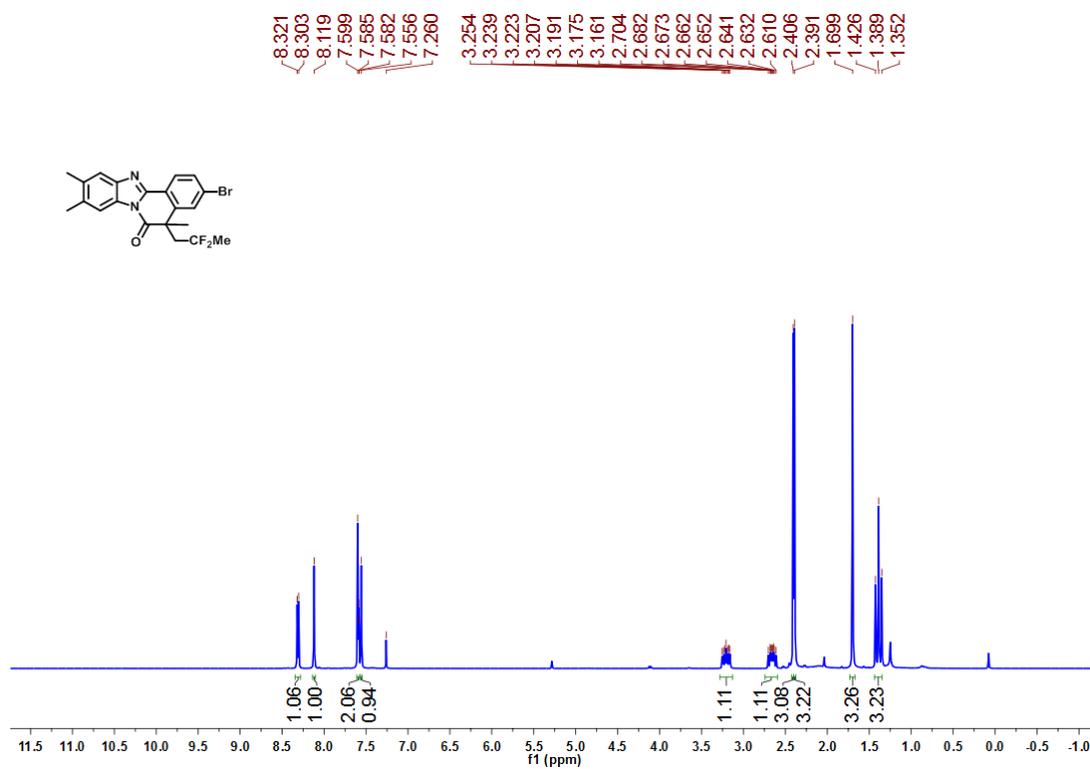
3q- $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3)



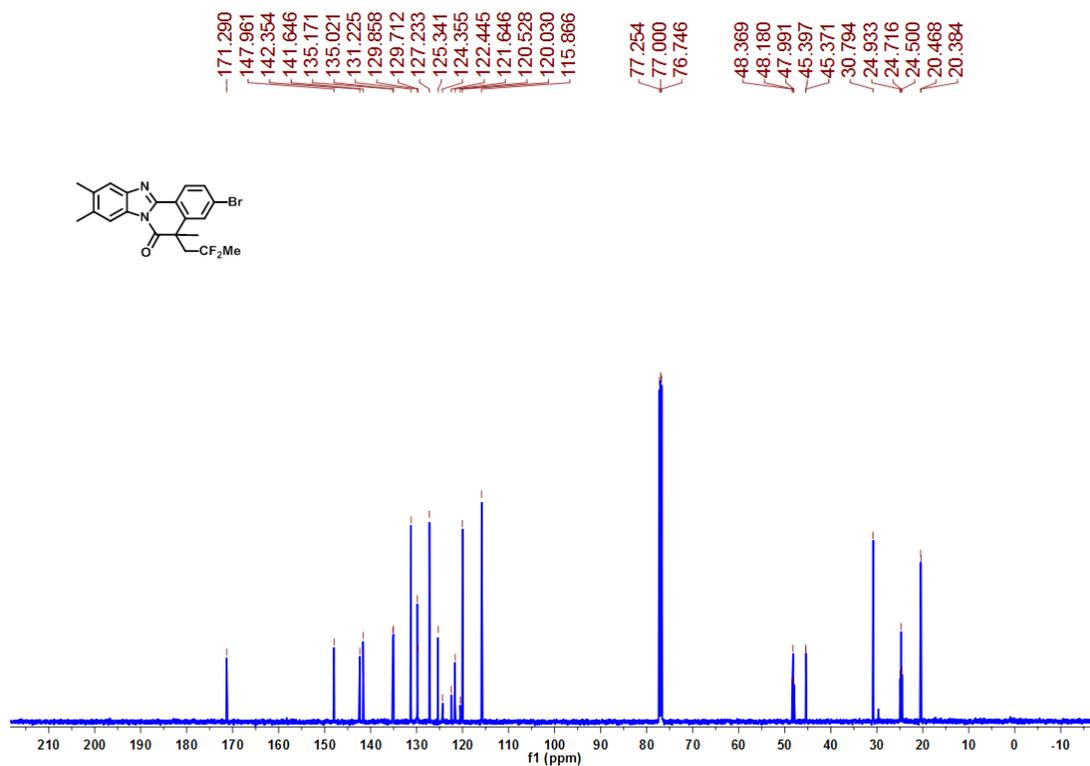
3q- ^{19}F NMR (471 MHz, CDCl_3)



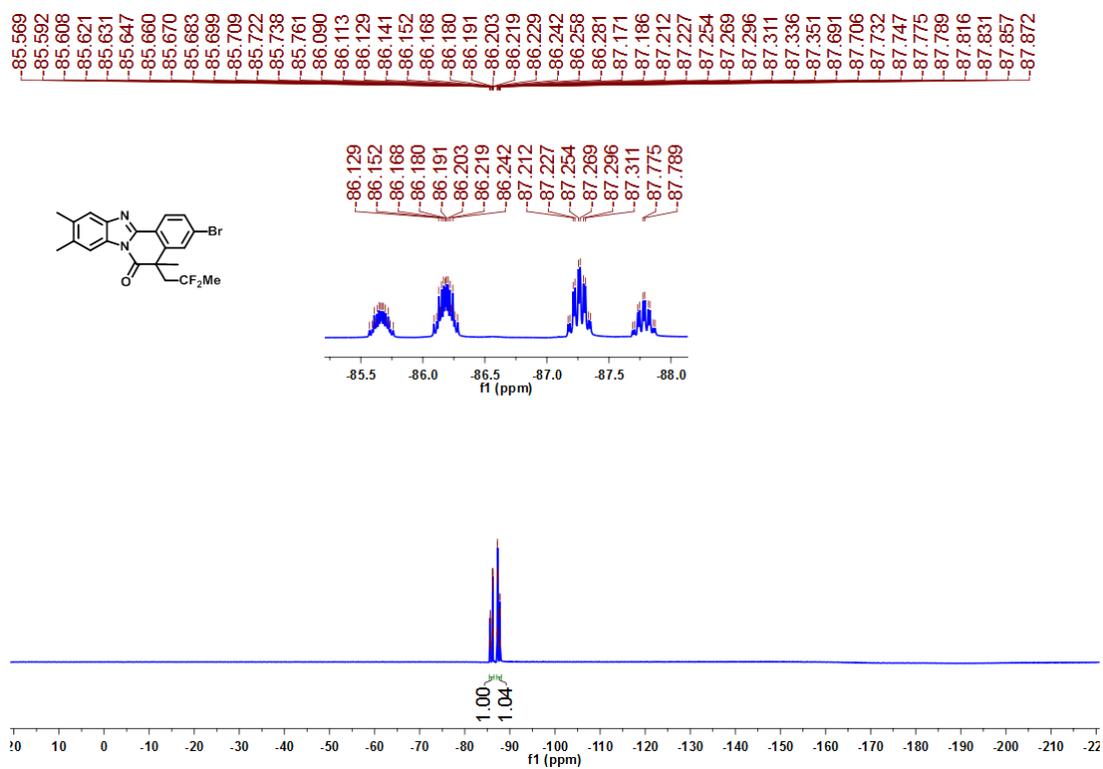
3r-¹H NMR (500 MHz, CDCl₃)



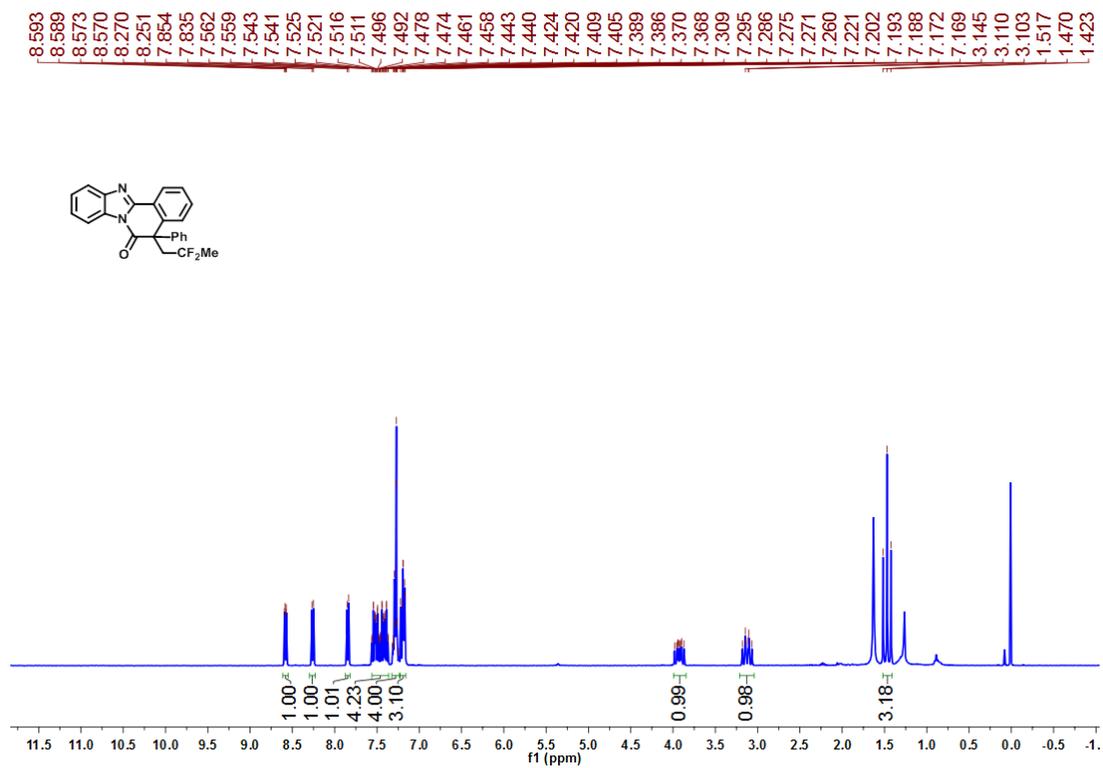
3r-¹³C{¹H} NMR (125 MHz, CDCl₃)



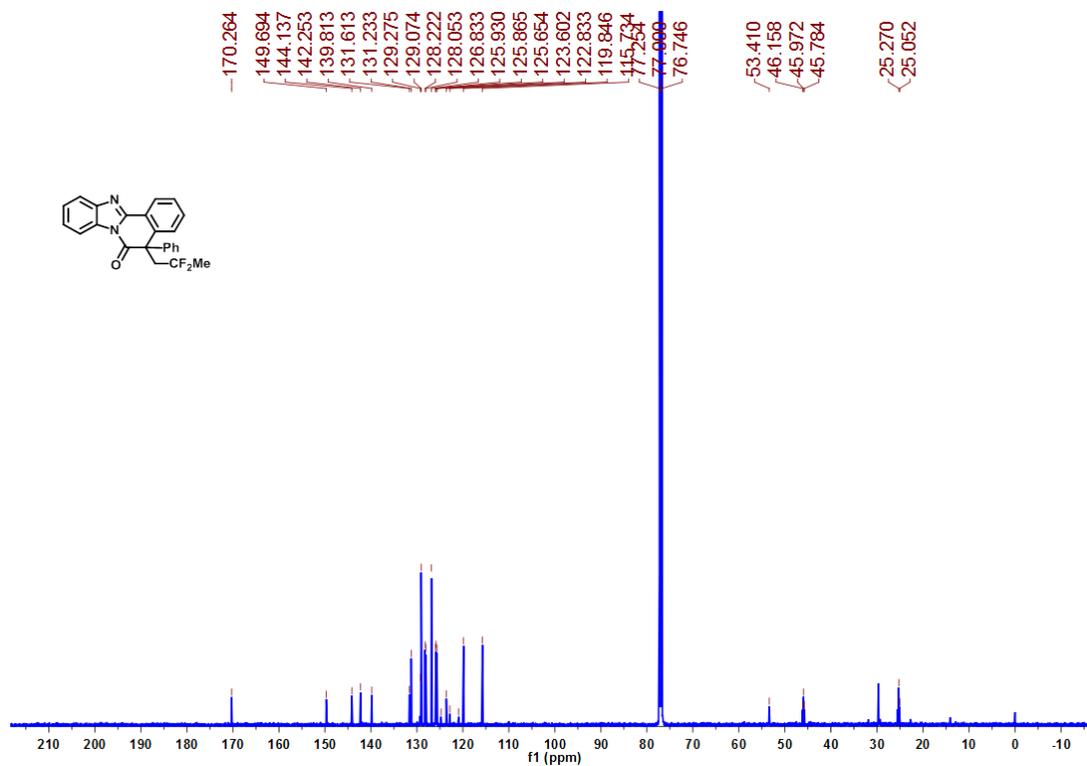
3r- ^{19}F NMR (471 MHz, CDCl_3)



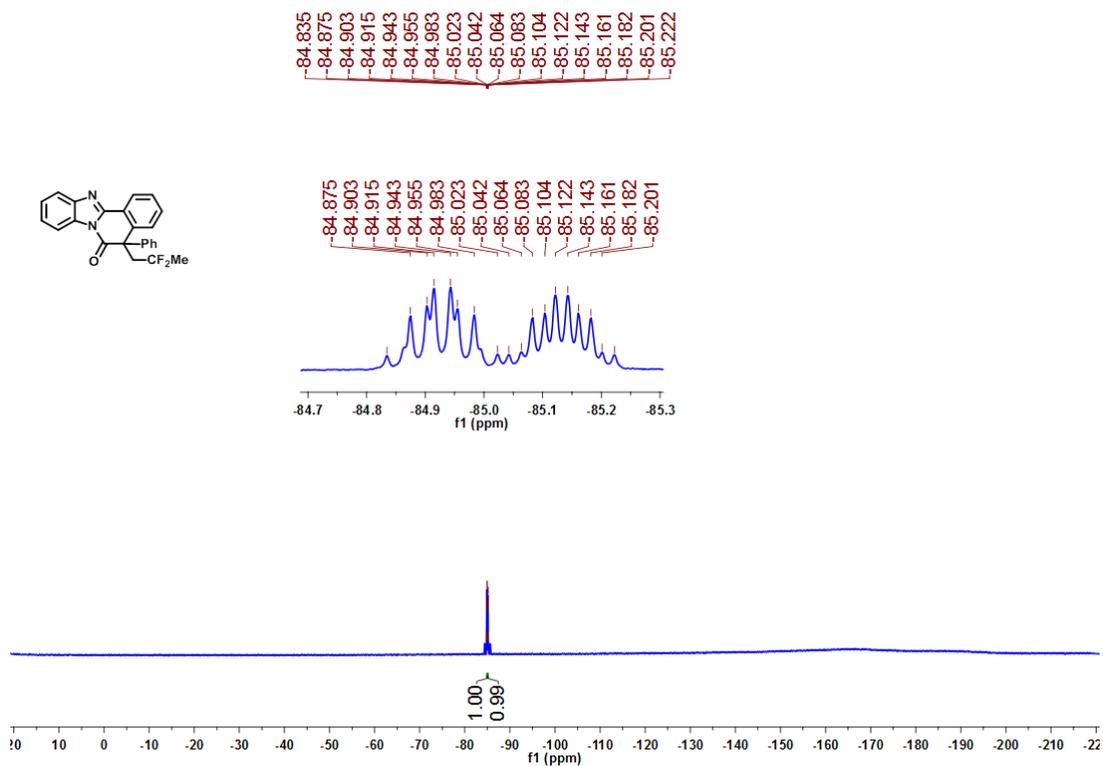
3s- ^1H NMR (400 MHz, CDCl_3)



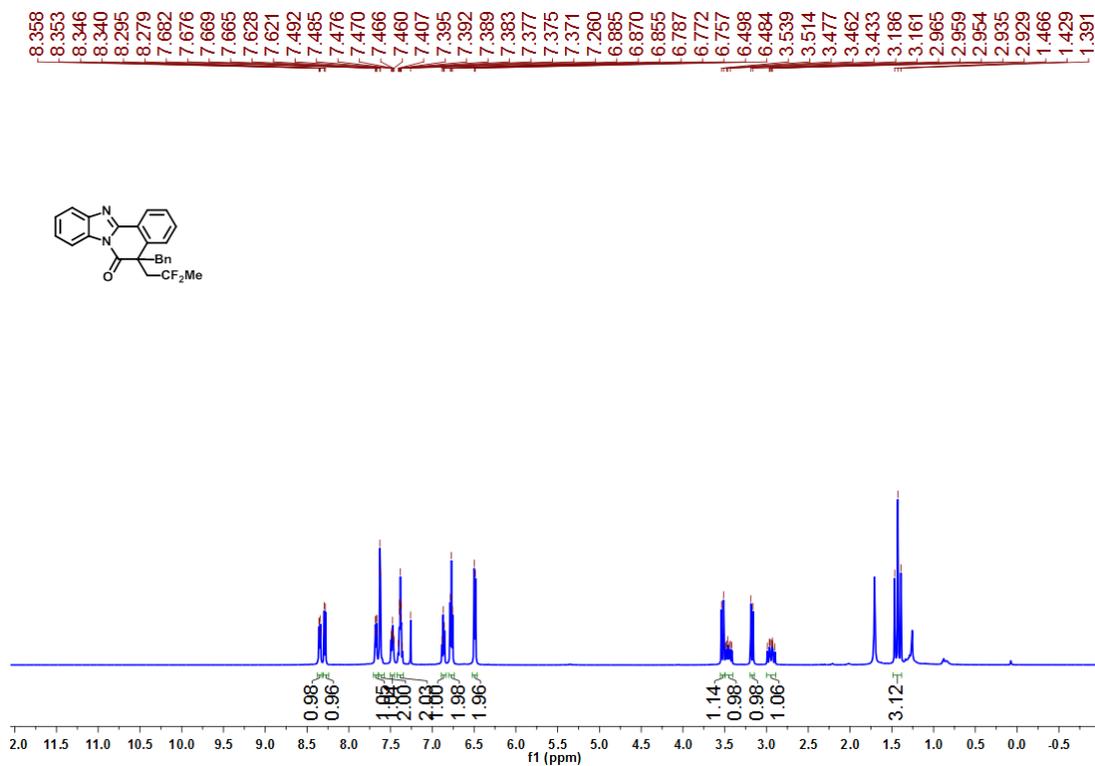
¹³C{¹H} NMR (125 MHz, CDCl₃)



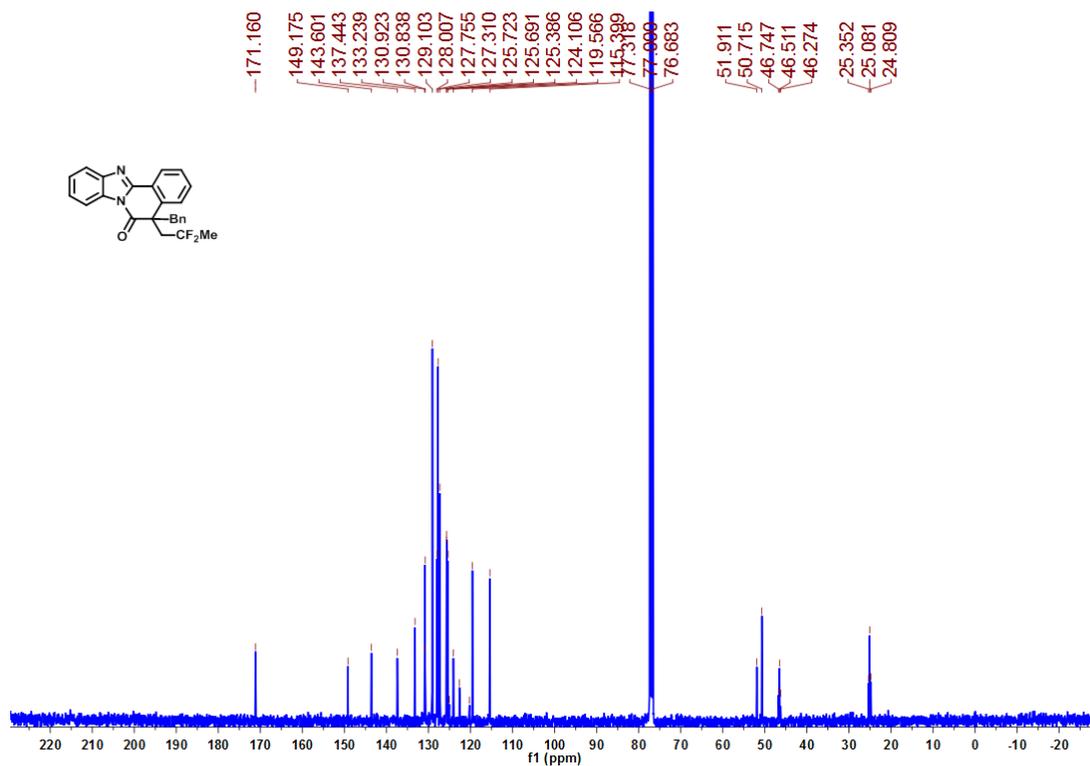
¹⁹F NMR (471 MHz, CDCl₃)



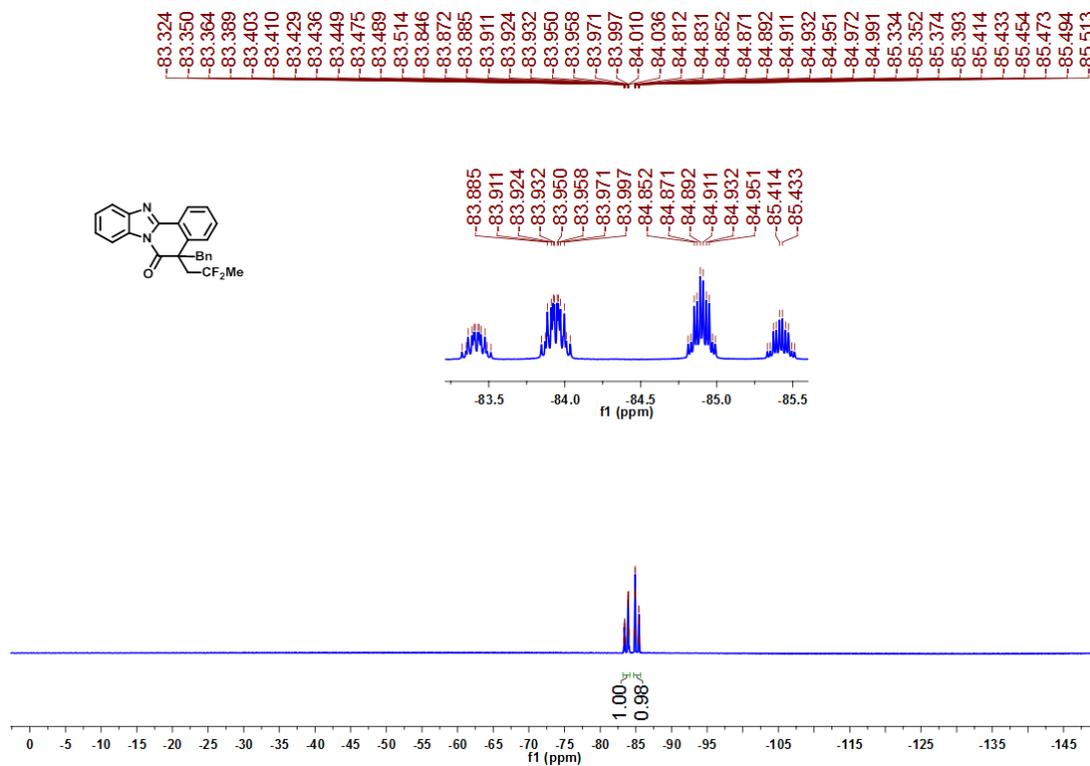
3t-¹H NMR (500 MHz, CDCl₃)



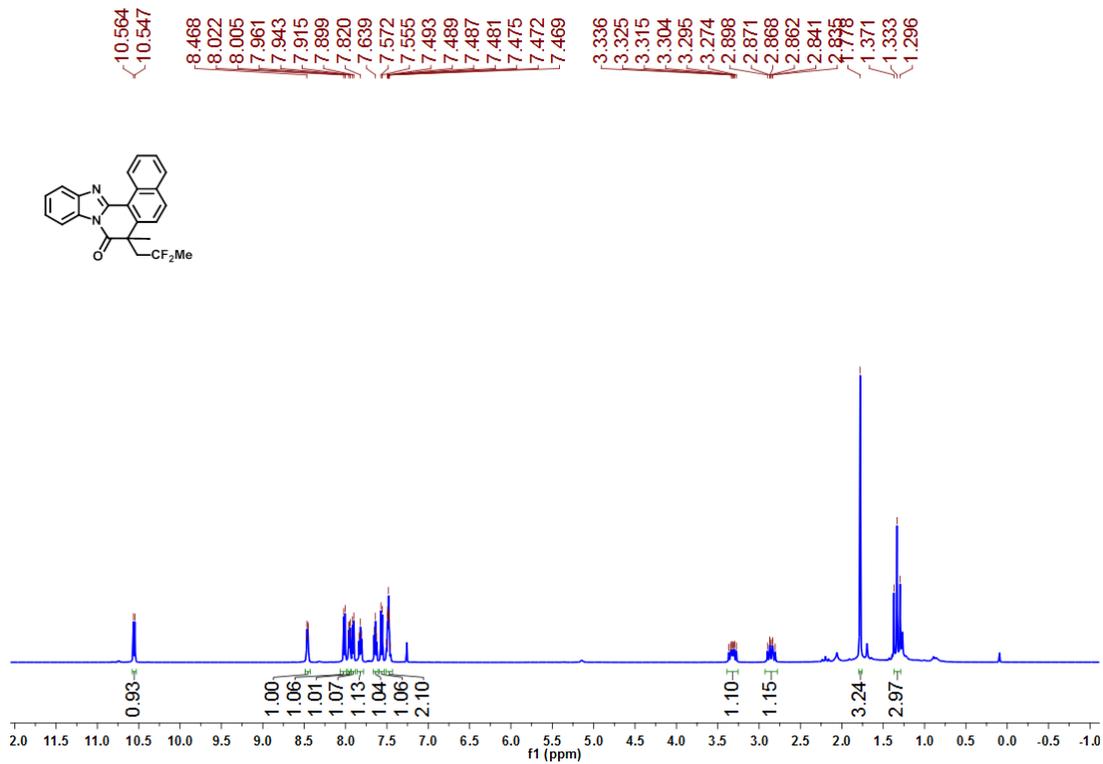
3t-¹³C{¹H} NMR (100 MHz, CDCl₃)



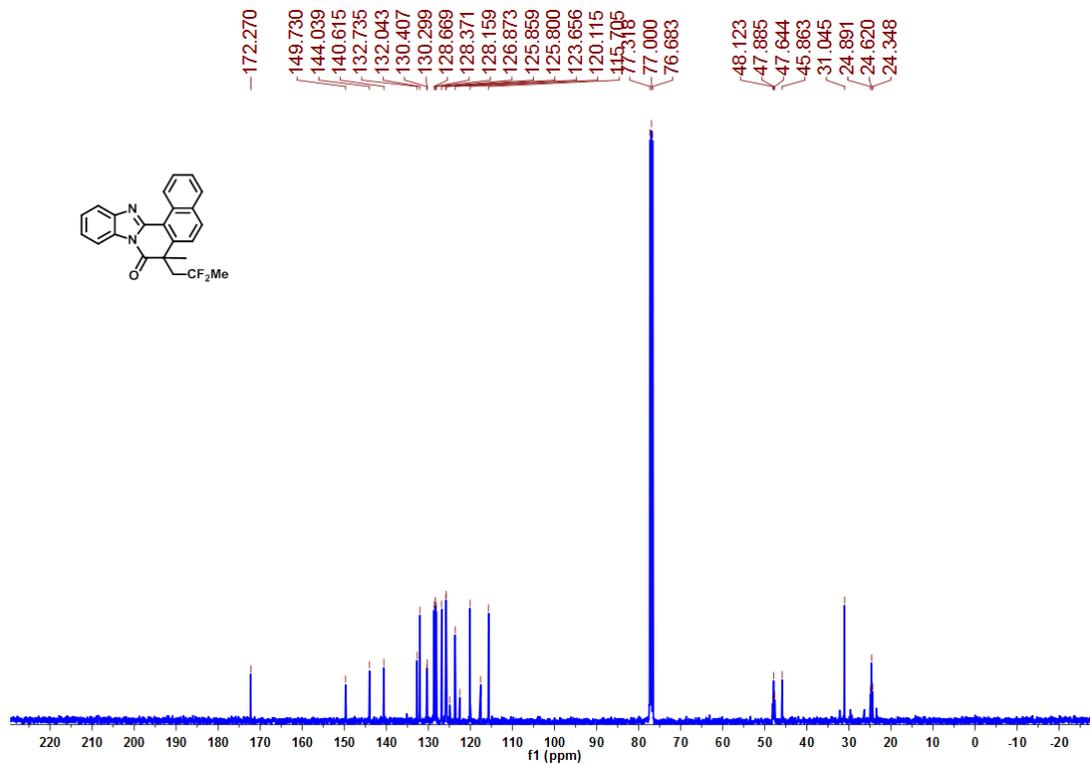
3t-¹⁹F NMR (471 MHz, CDCl₃)



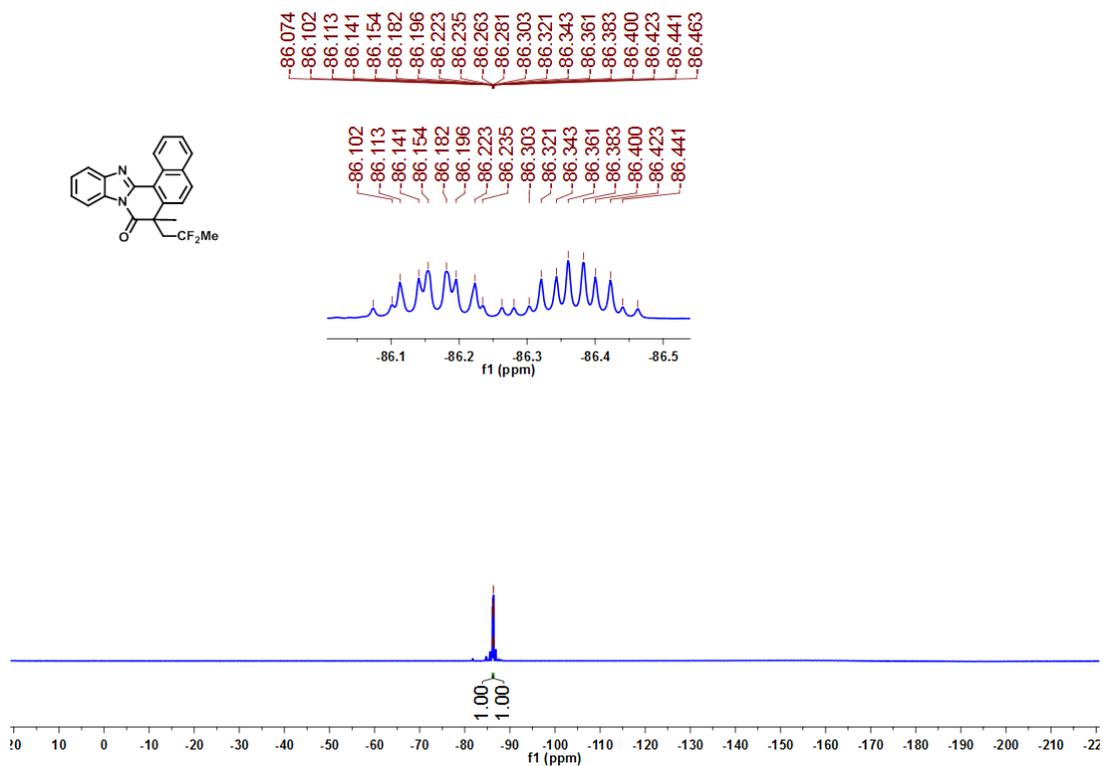
3u-¹H NMR (500 MHz, CDCl₃)



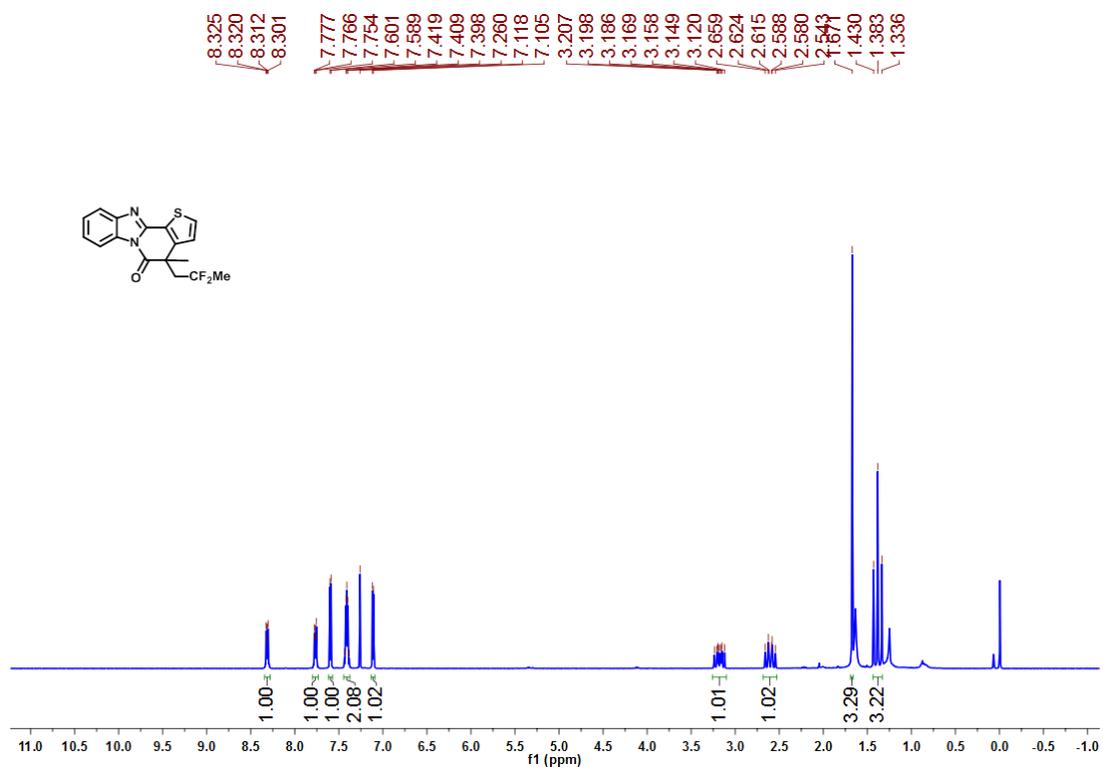
¹³C{¹H} NMR (100 MHz, CDCl₃)



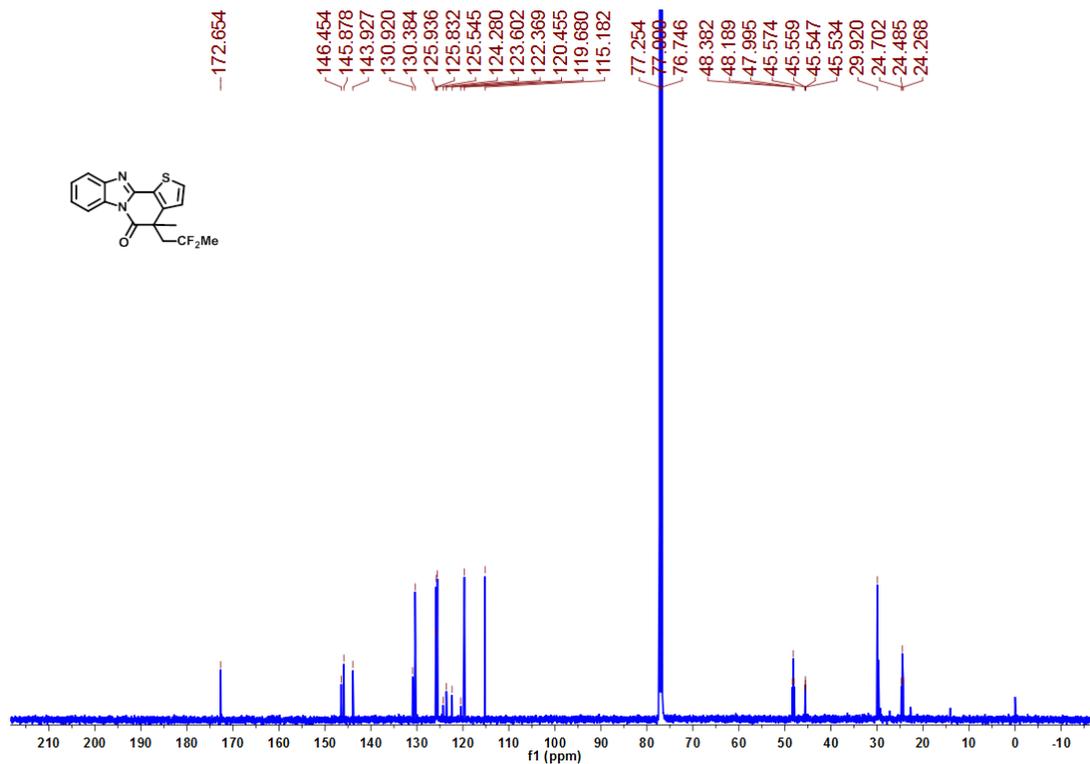
¹⁹F NMR (471 MHz, CDCl₃)



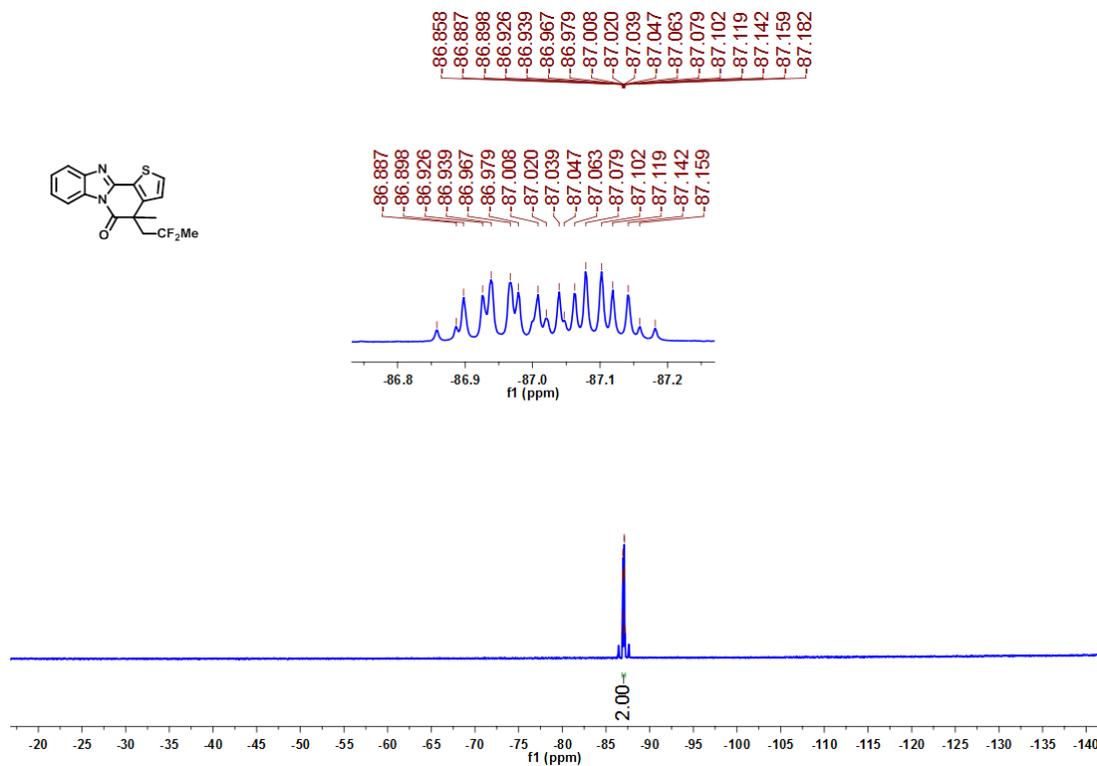
3v-¹H NMR (400 MHz, CDCl₃)



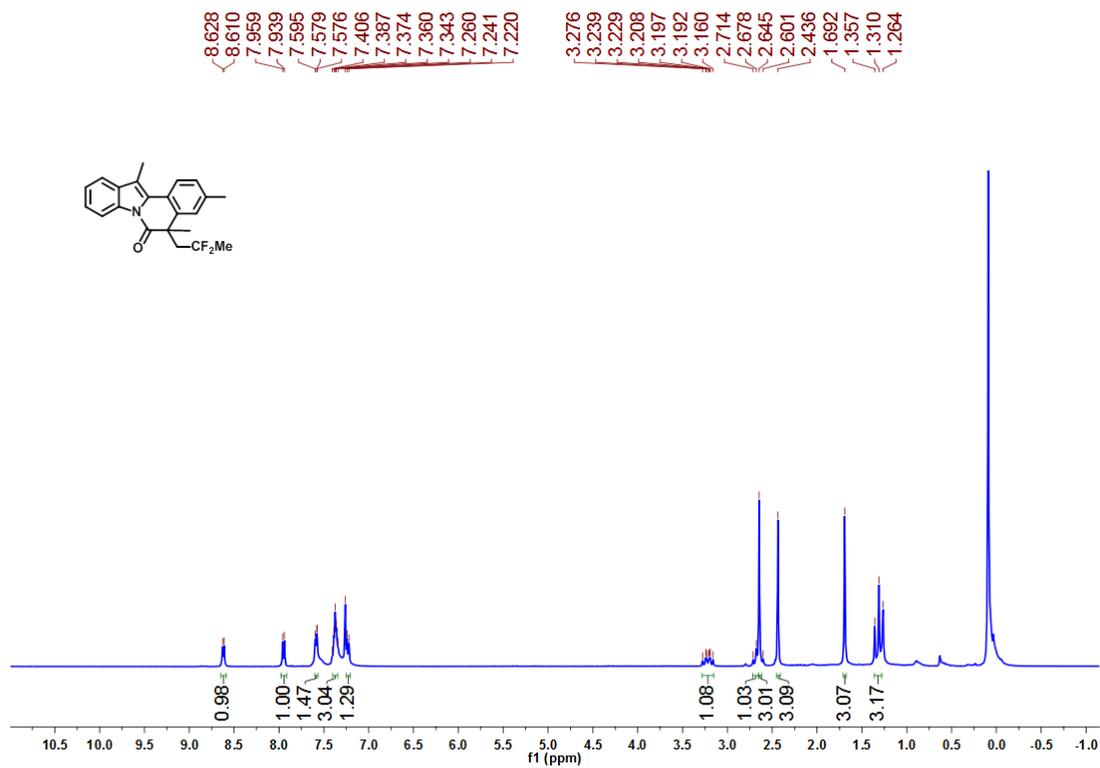
3v-¹³C{¹H} NMR (125 MHz, CDCl₃)



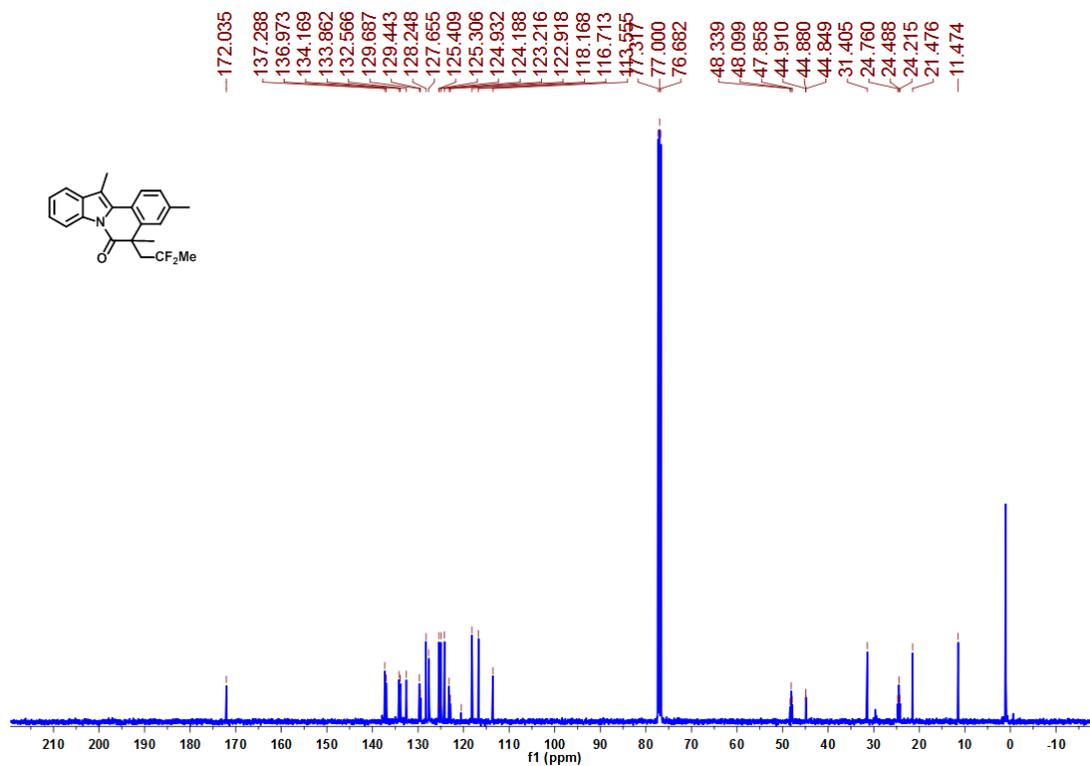
3v-¹⁹F NMR (471 MHz, CDCl₃)



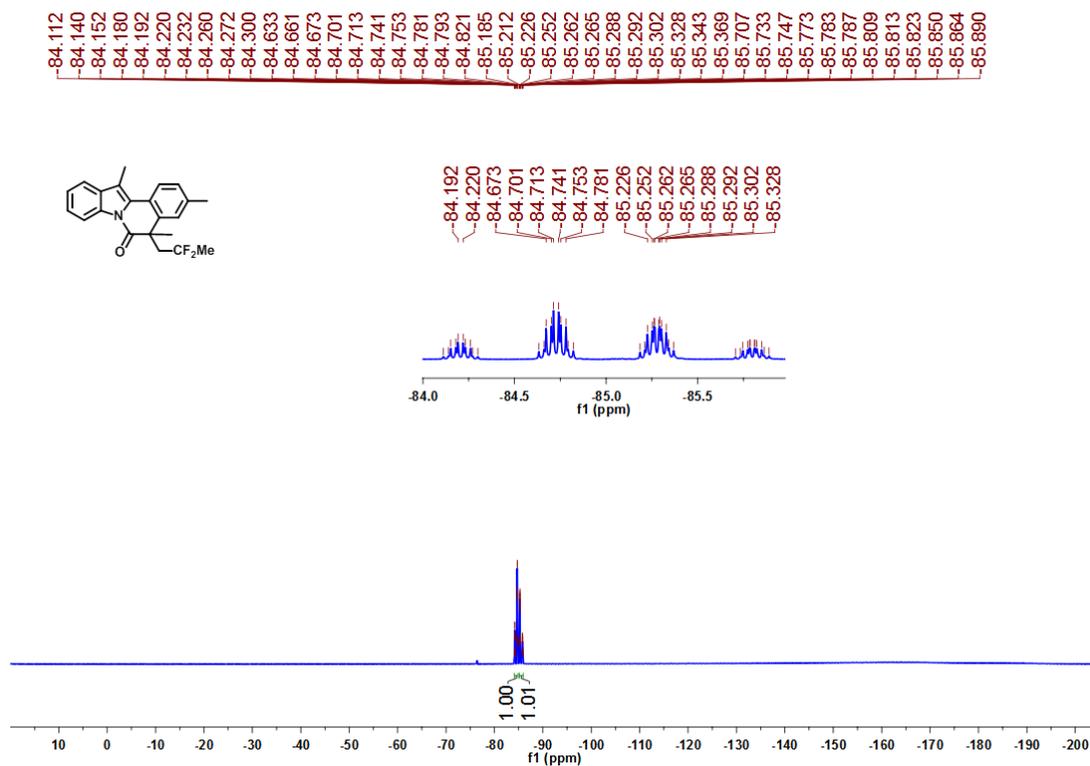
5a-¹H NMR (500 MHz, CDCl₃)



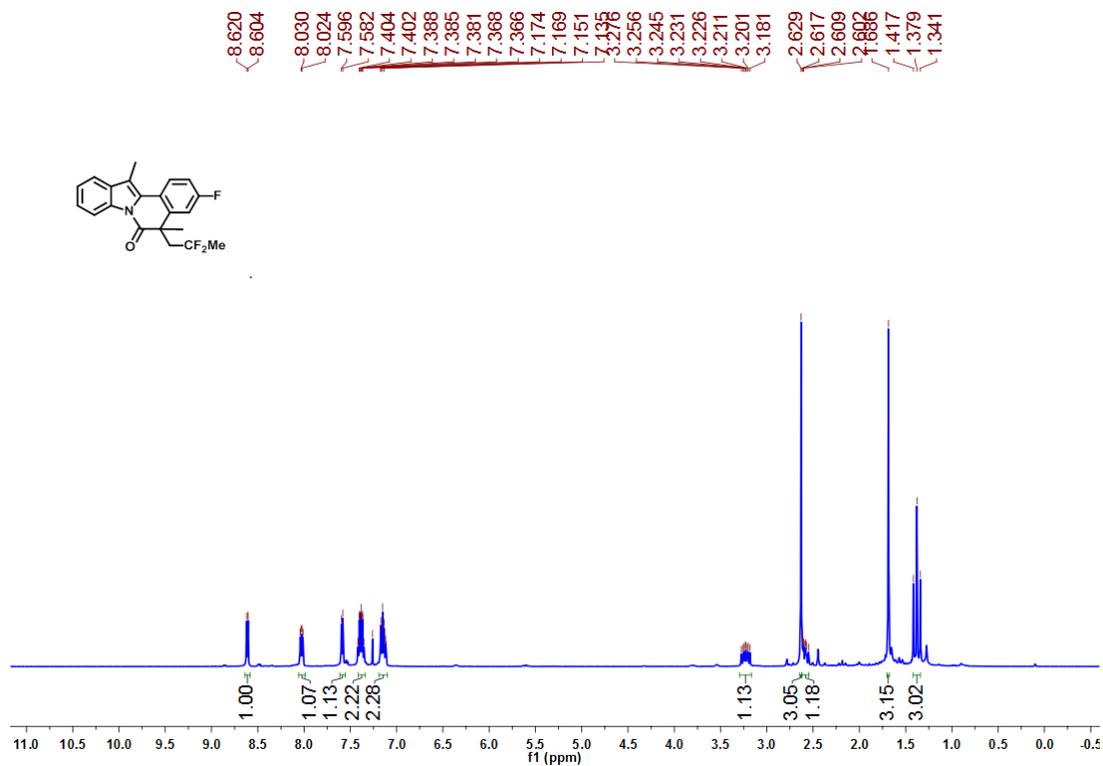
5a-¹³C{¹H} NMR (125 MHz, CDCl₃)



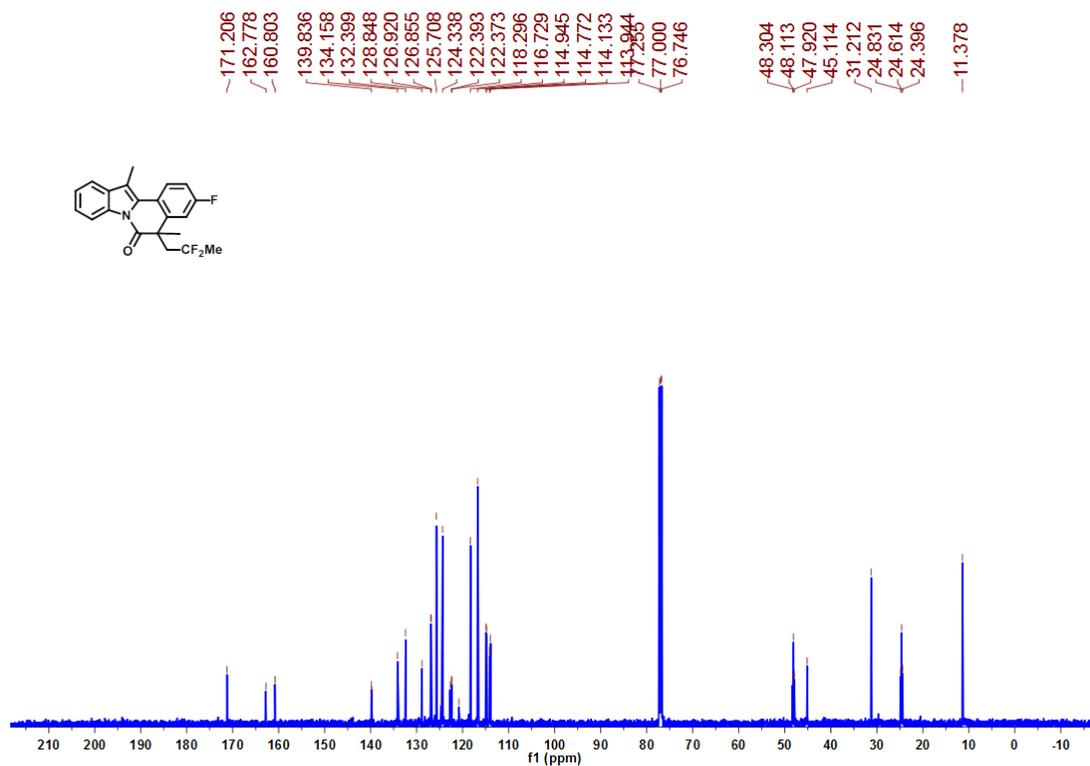
5a-¹⁹F NMR (471 MHz, CDCl₃)



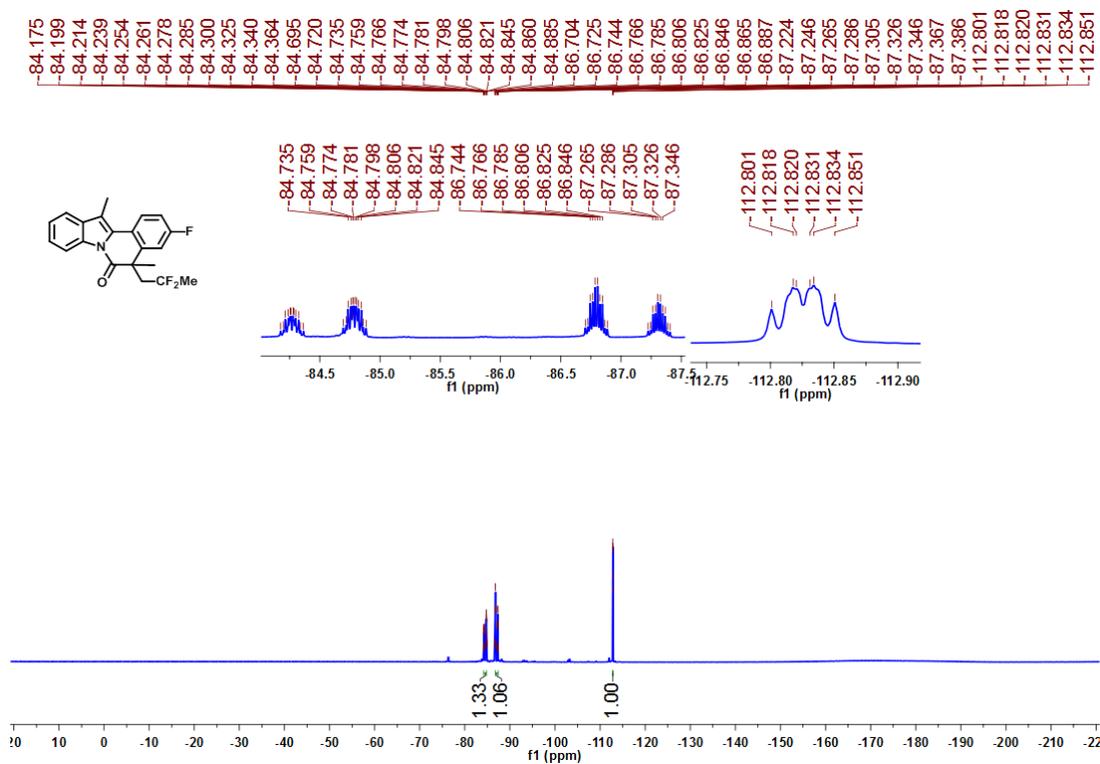
5b-¹H NMR (500 MHz, CDCl₃)



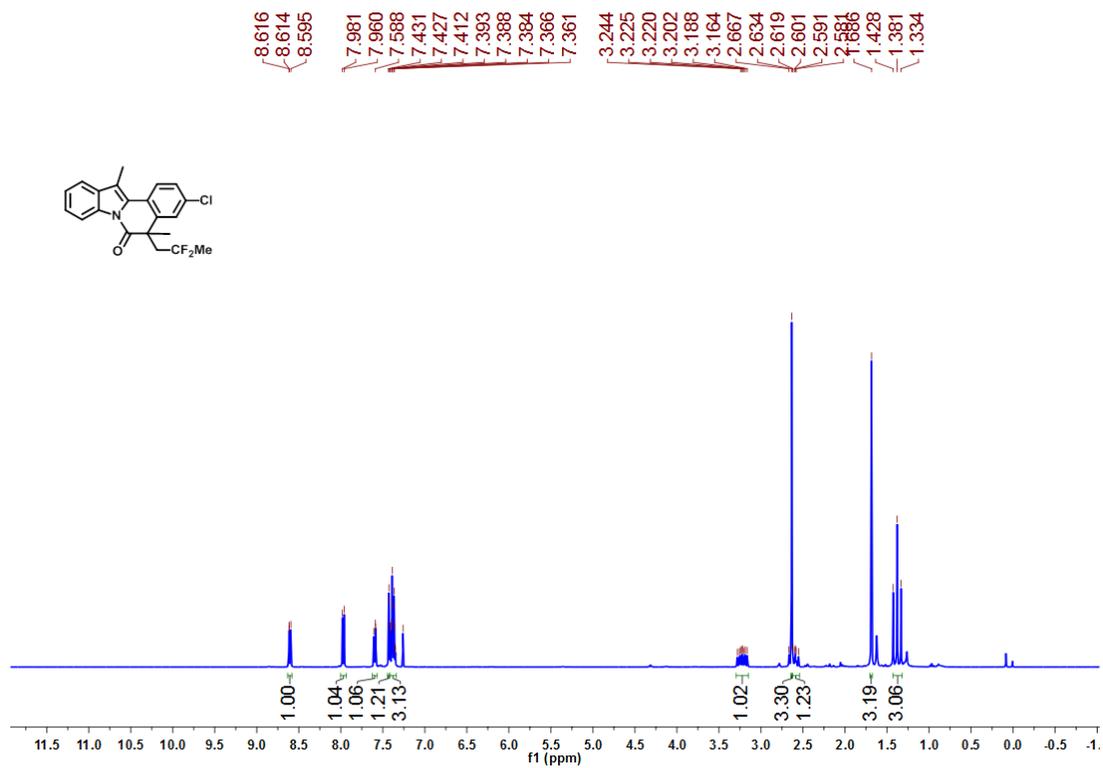
5b-¹³C{¹H} NMR (125 MHz, CDCl₃)



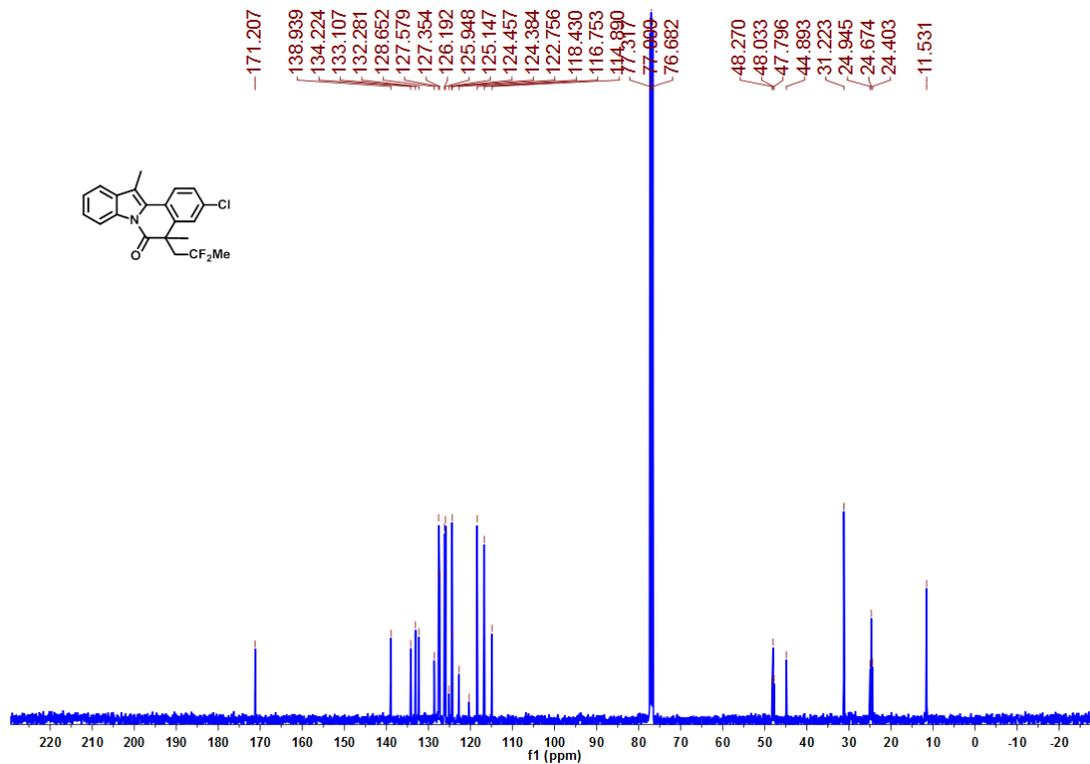
5b-¹⁹F NMR (471 MHz, CDCl₃)



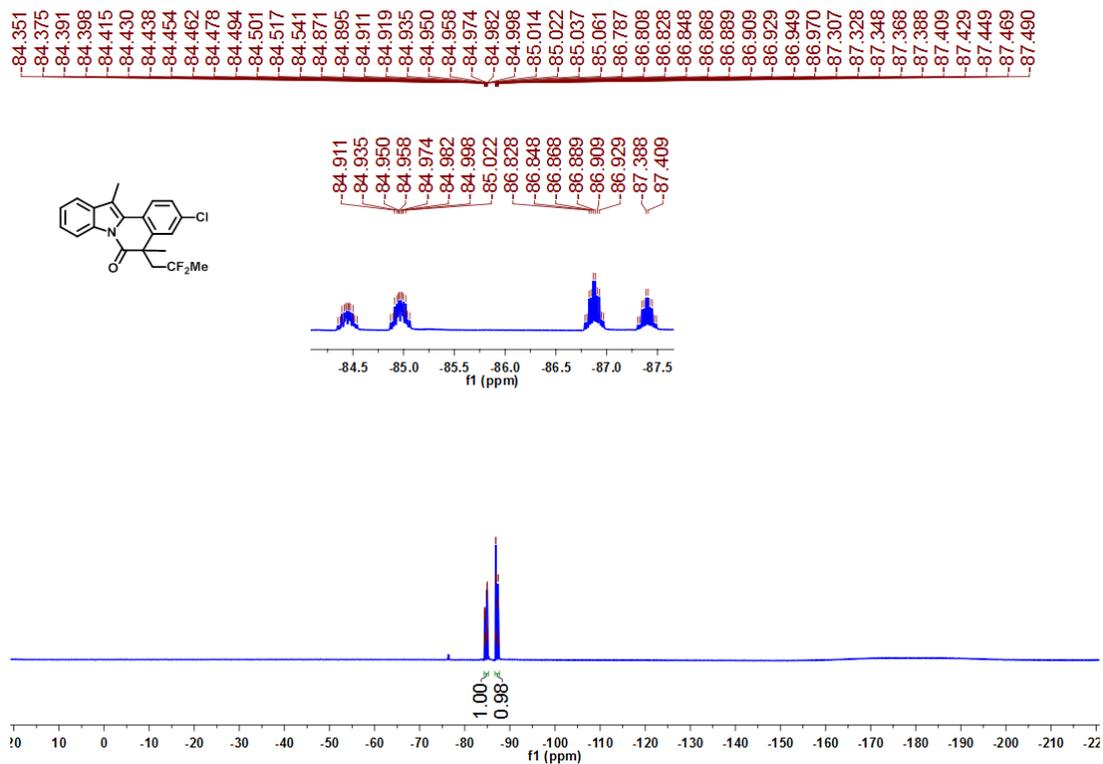
5c-¹H NMR (400 MHz, CDCl₃)



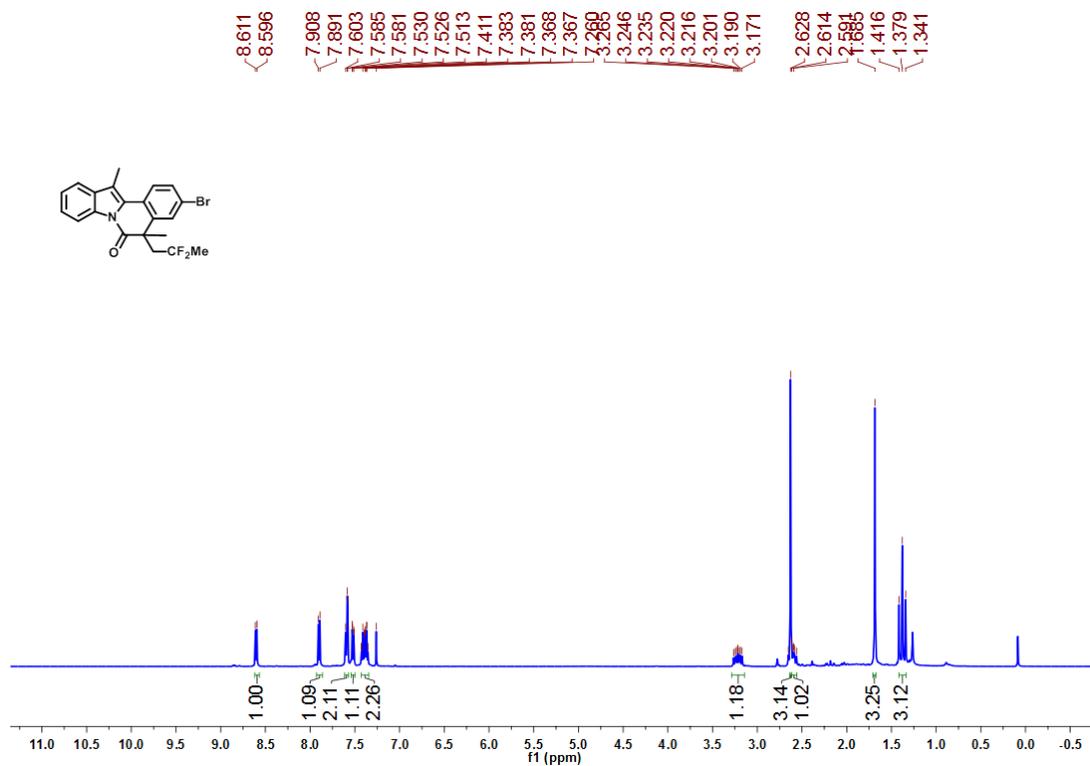
5c-¹³C{¹H} NMR (100 MHz, CDCl₃)



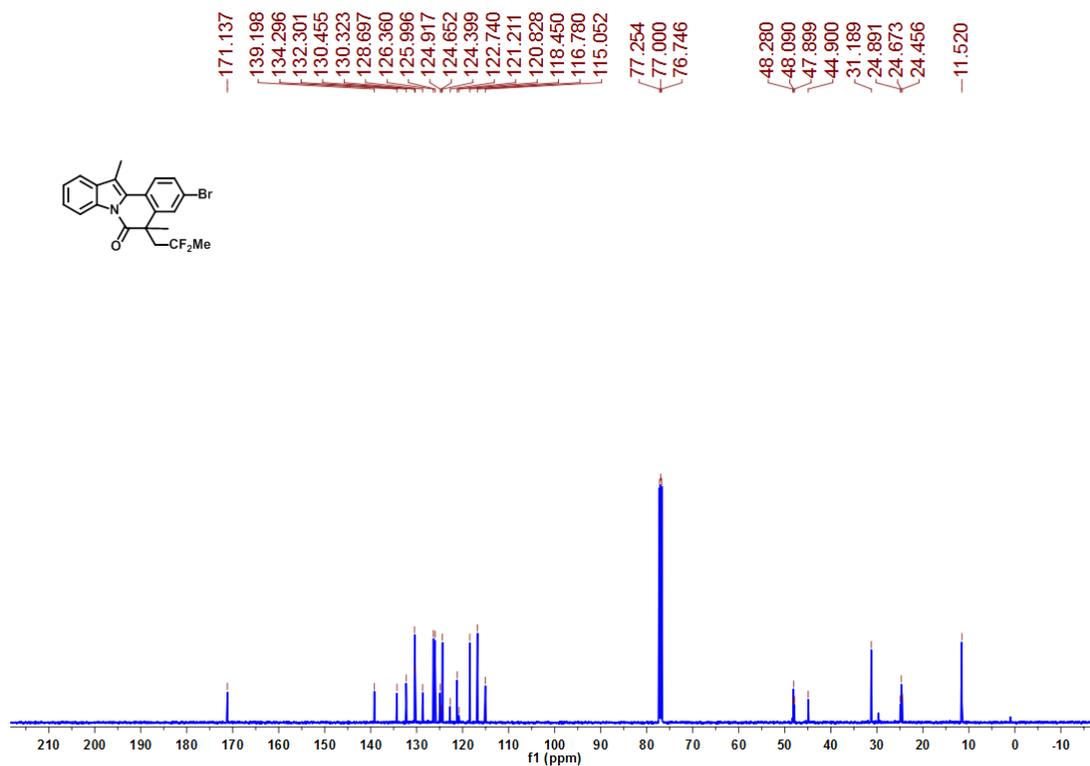
5c-¹⁹F NMR (471 MHz, CDCl₃)



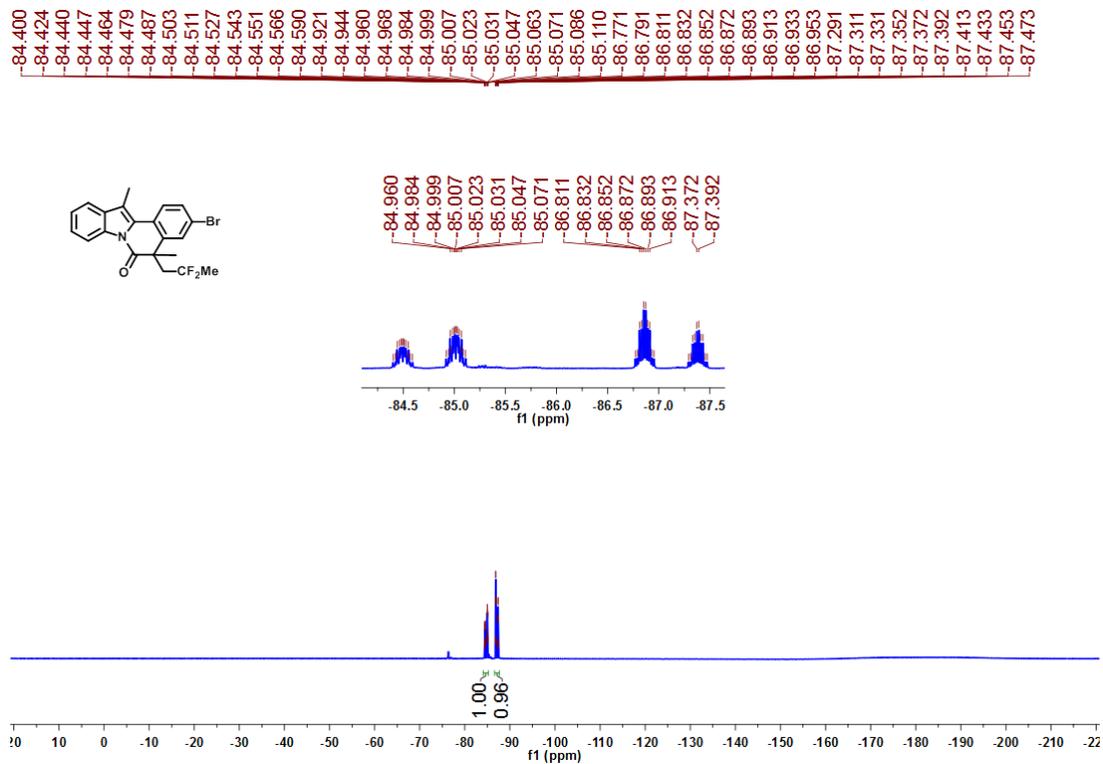
5d- ^1H NMR (500 MHz, CDCl_3)



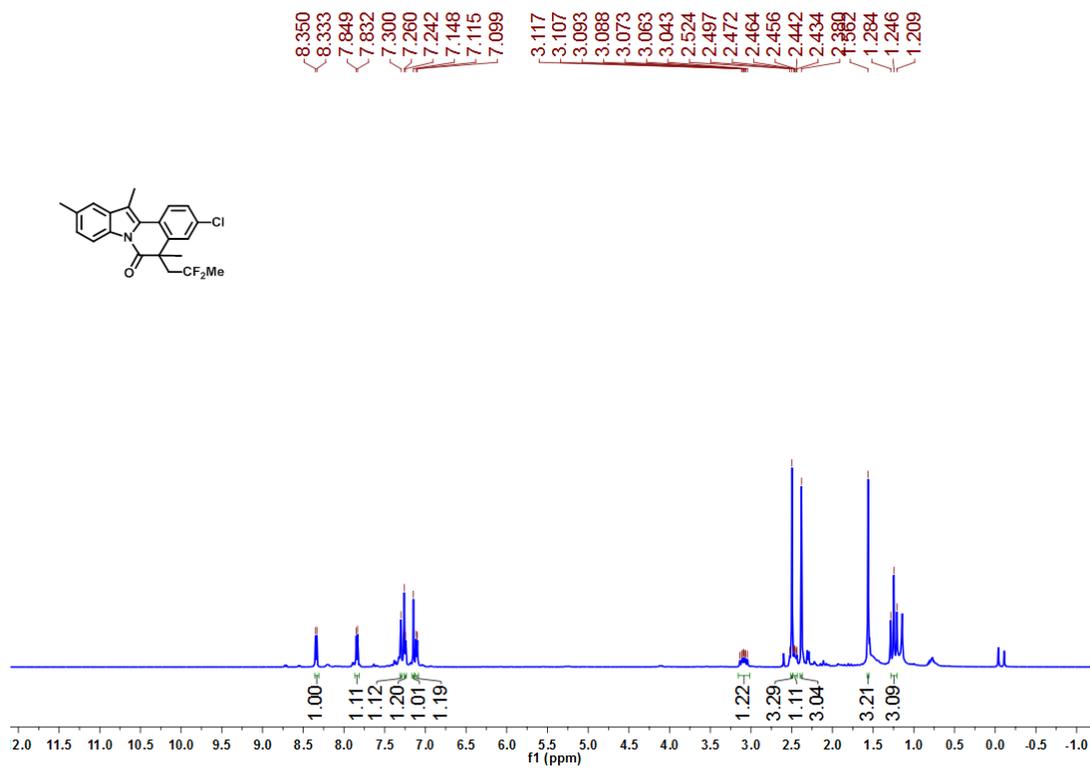
5d- $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3)



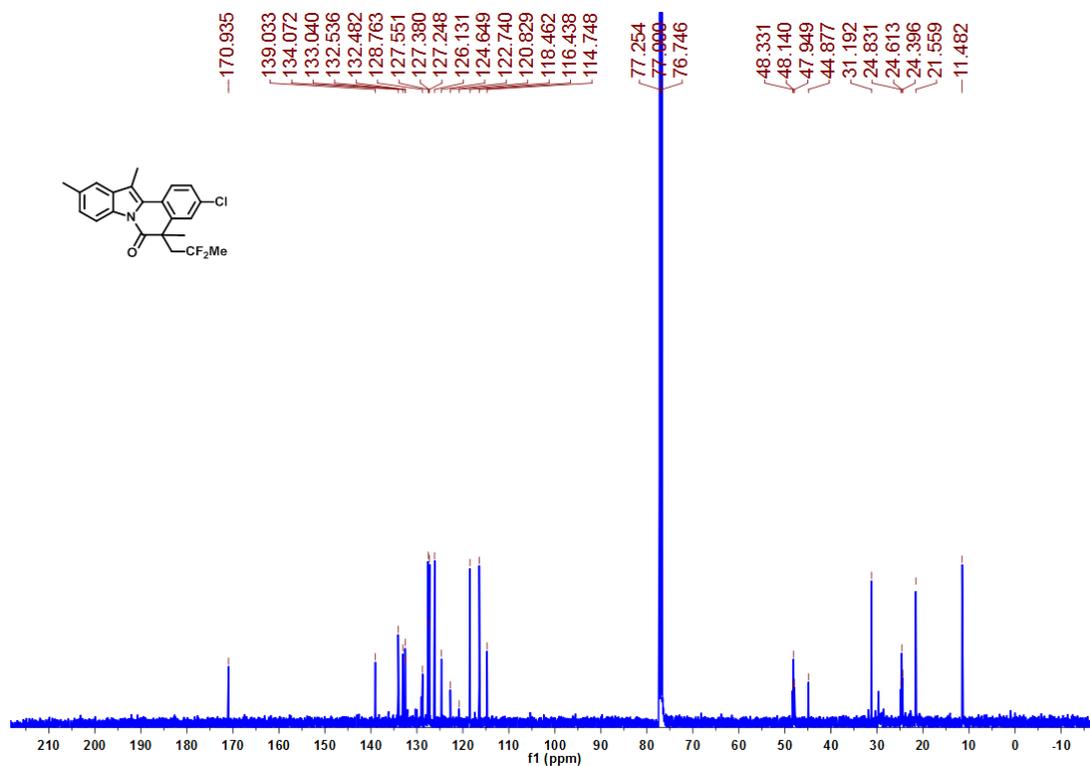
5d-¹⁹F NMR (471 MHz, CDCl₃)



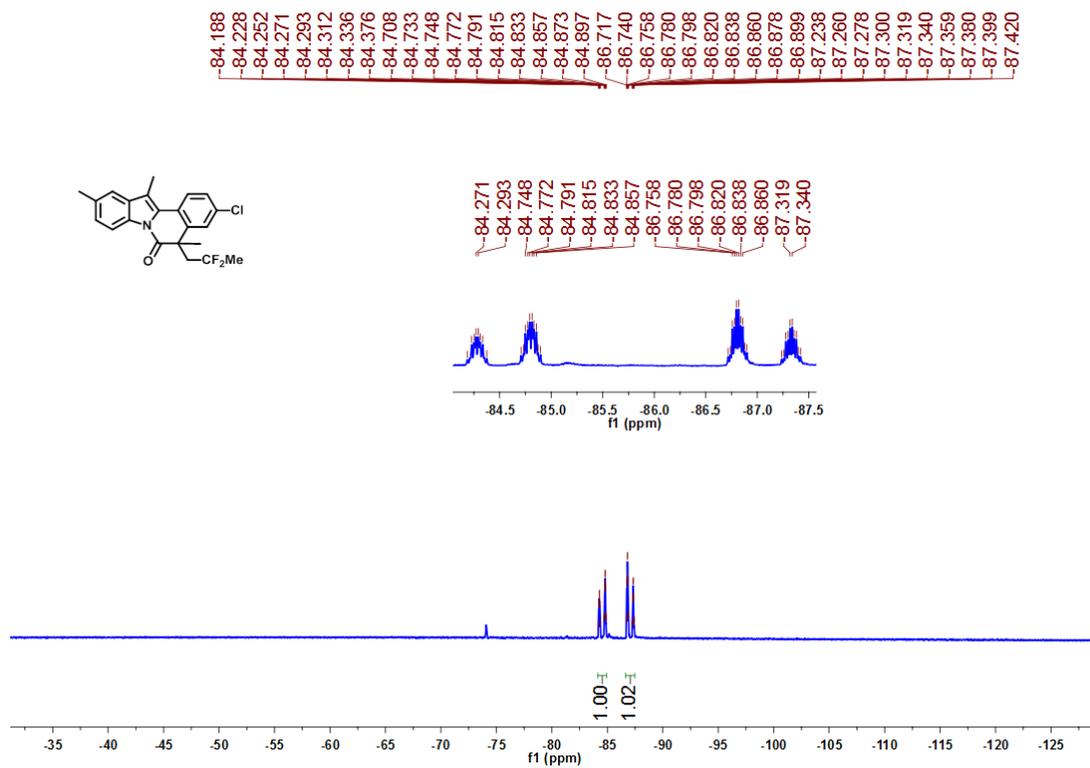
5e-¹H NMR (500 MHz, CDCl₃)



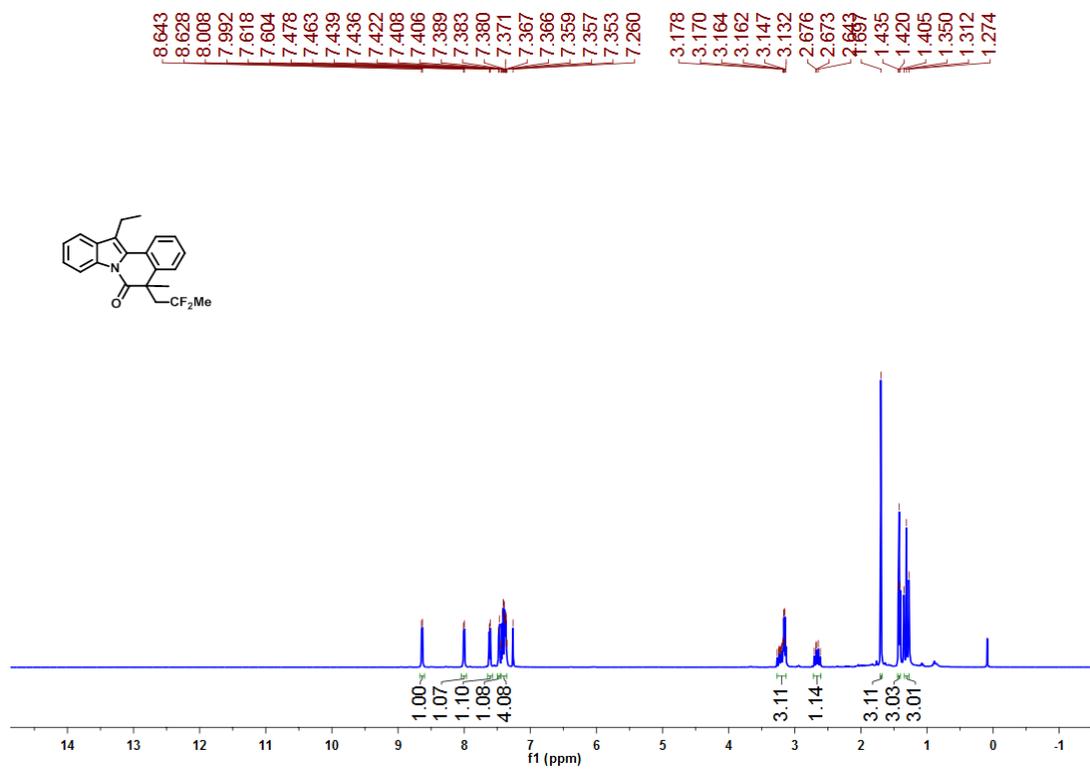
5e-¹³C{¹H} NMR (125 MHz, CDCl₃)



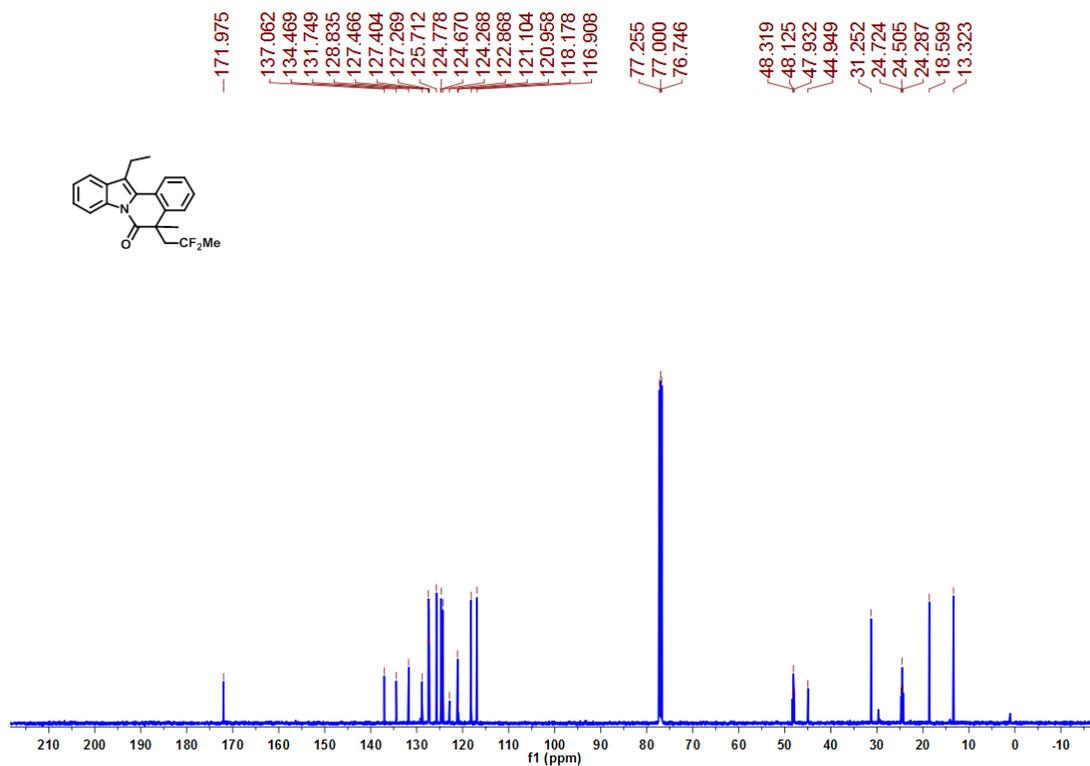
5e-¹⁹F NMR (471 MHz, CDCl₃)



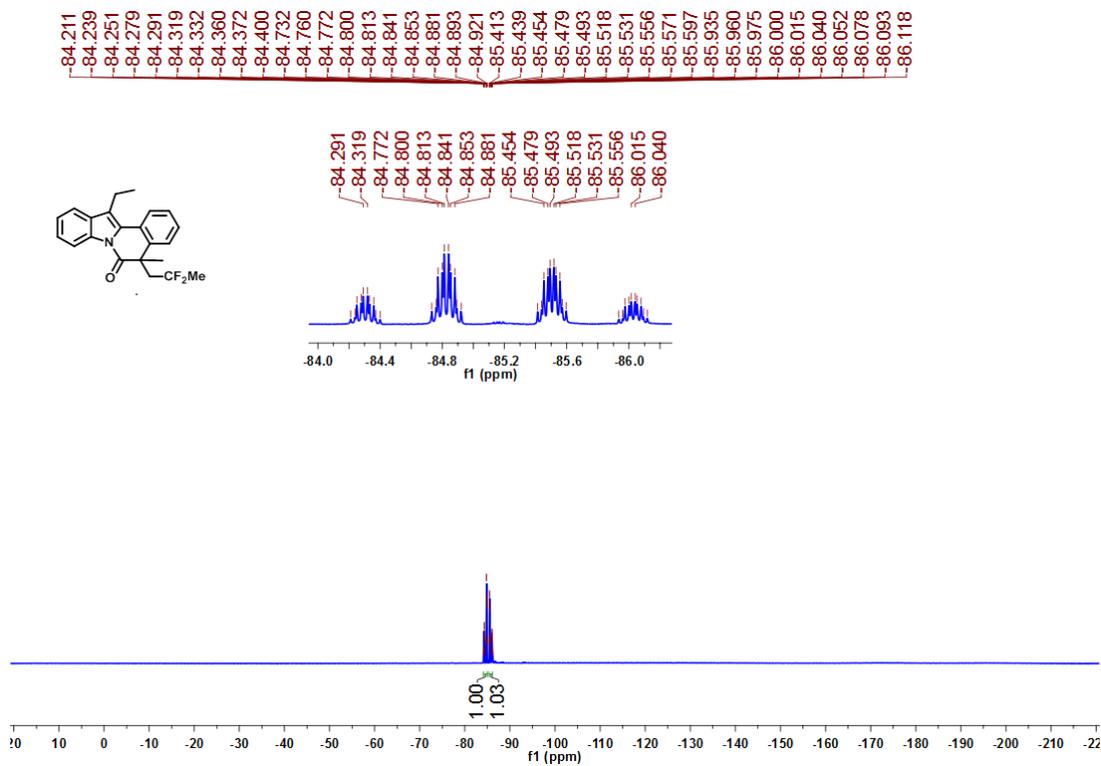
5f-¹H NMR (500 MHz, CDCl₃)



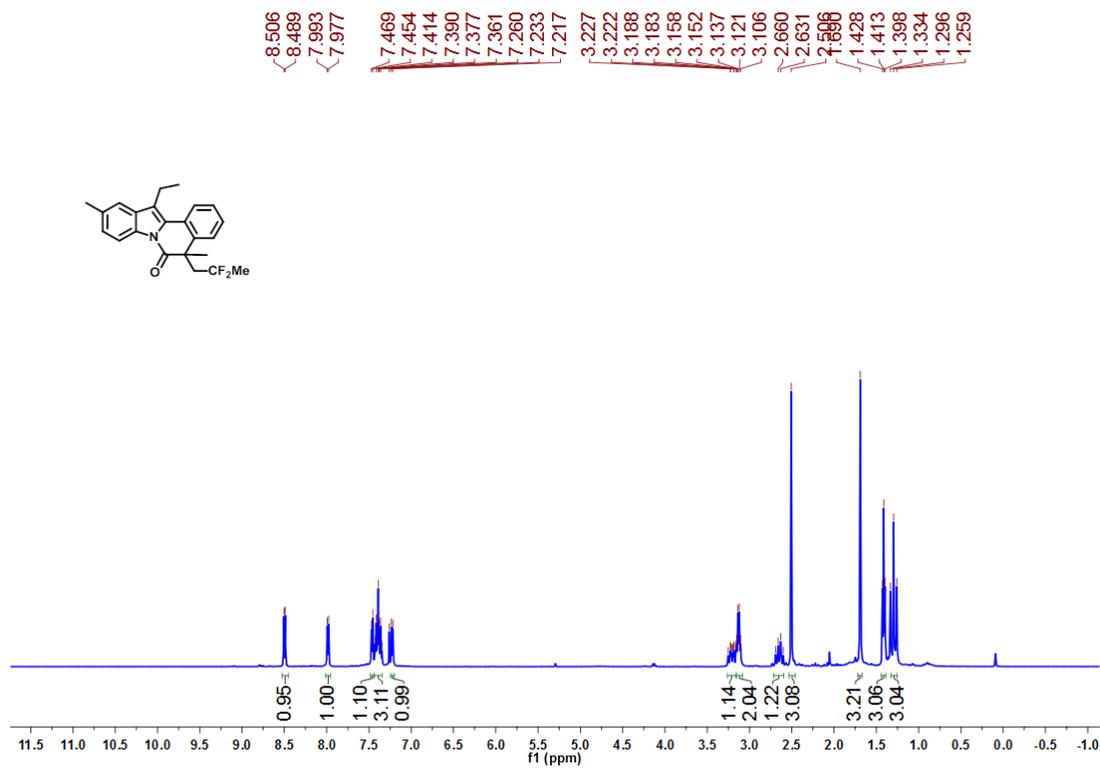
5f-¹³C{¹H} NMR (125 MHz, CDCl₃)



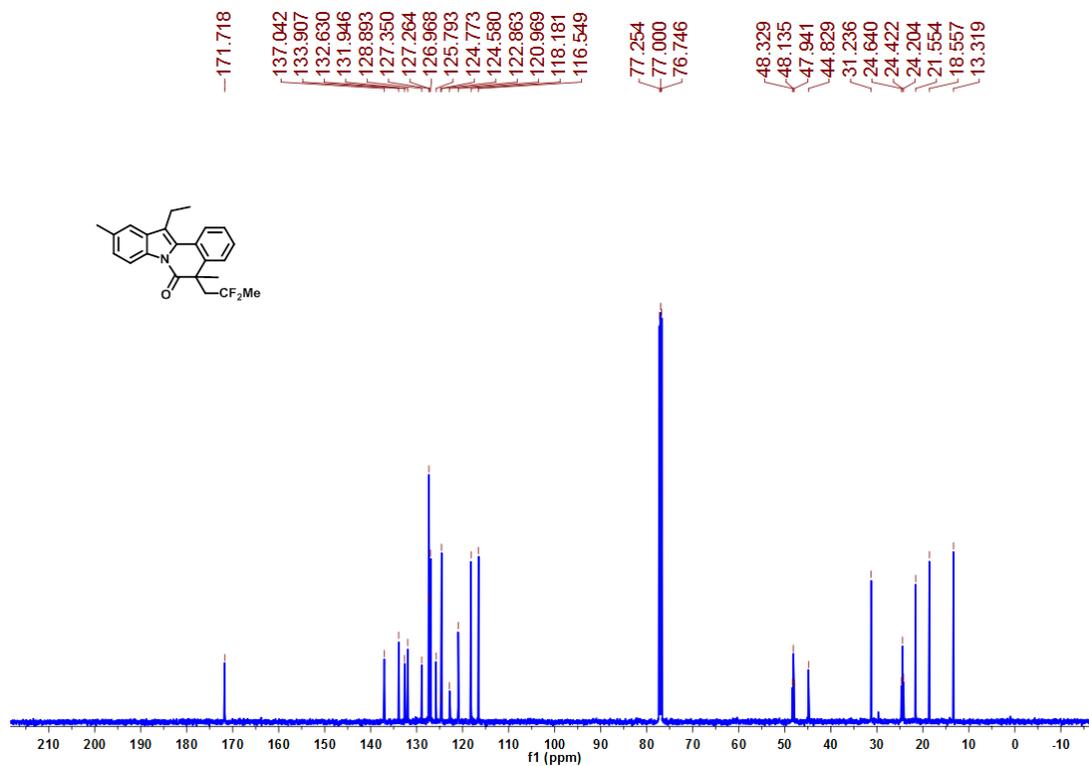
5f-¹⁹F NMR (471 MHz, CDCl₃)



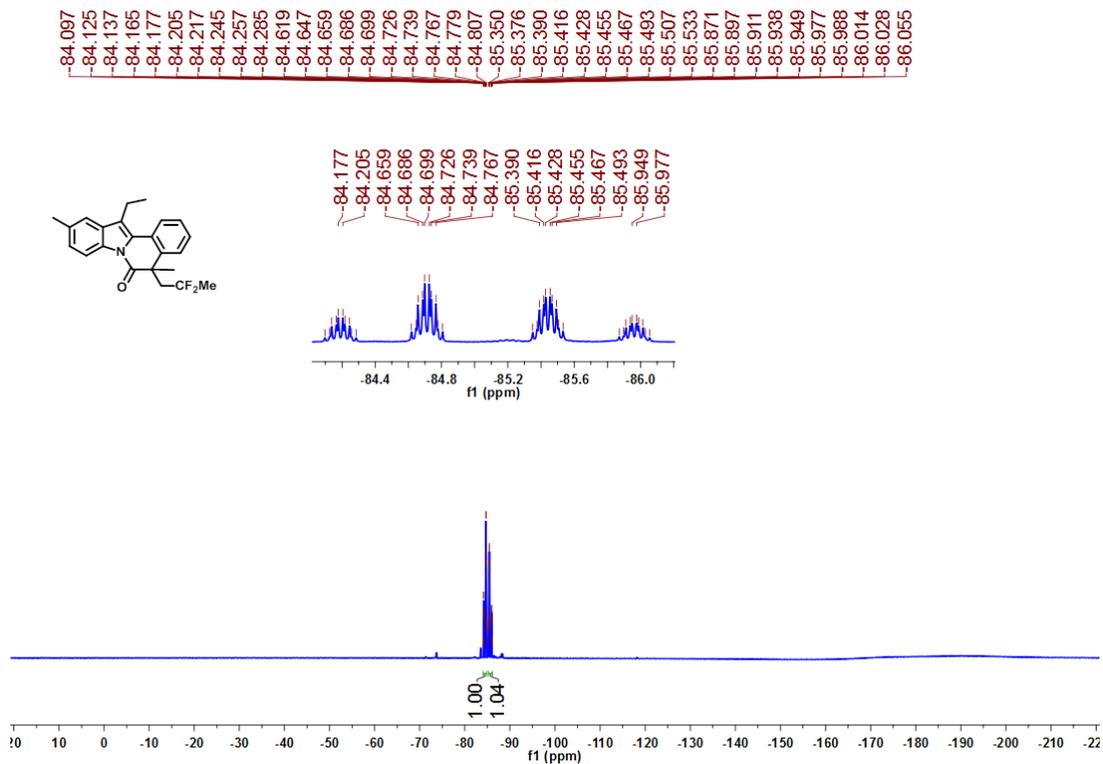
5g-¹H NMR (500 MHz, CDCl₃)



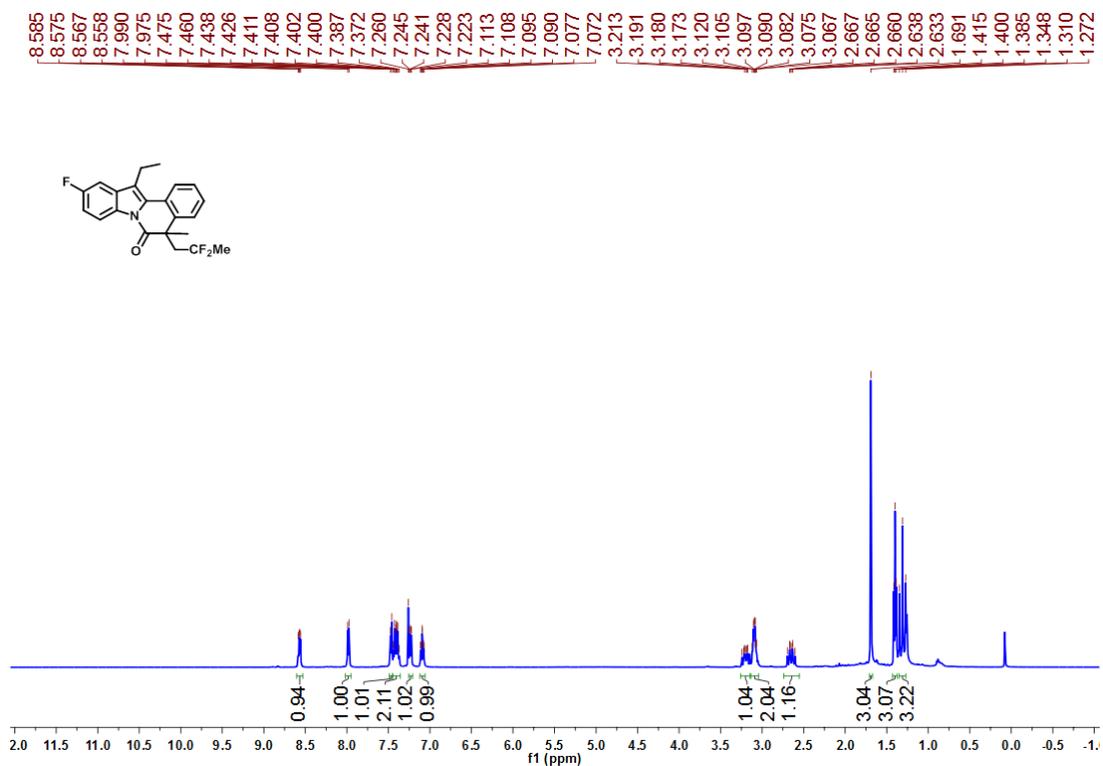
5g-¹³C{¹H} NMR (125 MHz, CDCl₃)



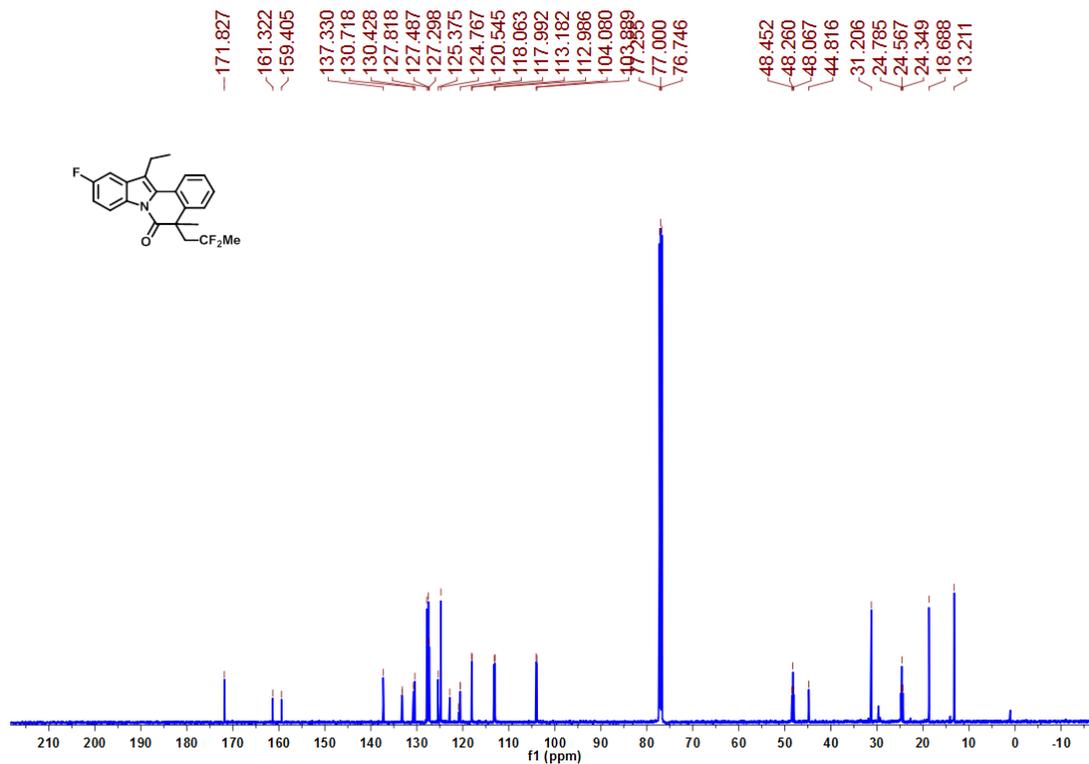
5g-¹⁹F NMR (471 MHz, CDCl₃)



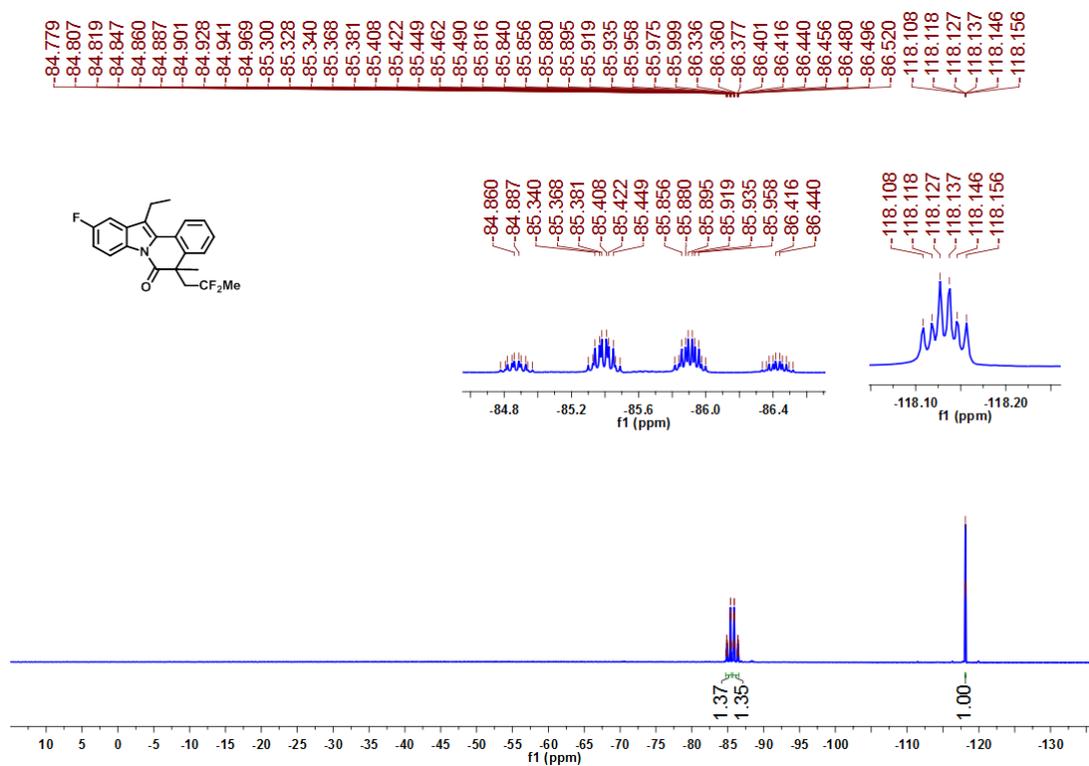
5h- ^1H NMR (500 MHz, CDCl_3)



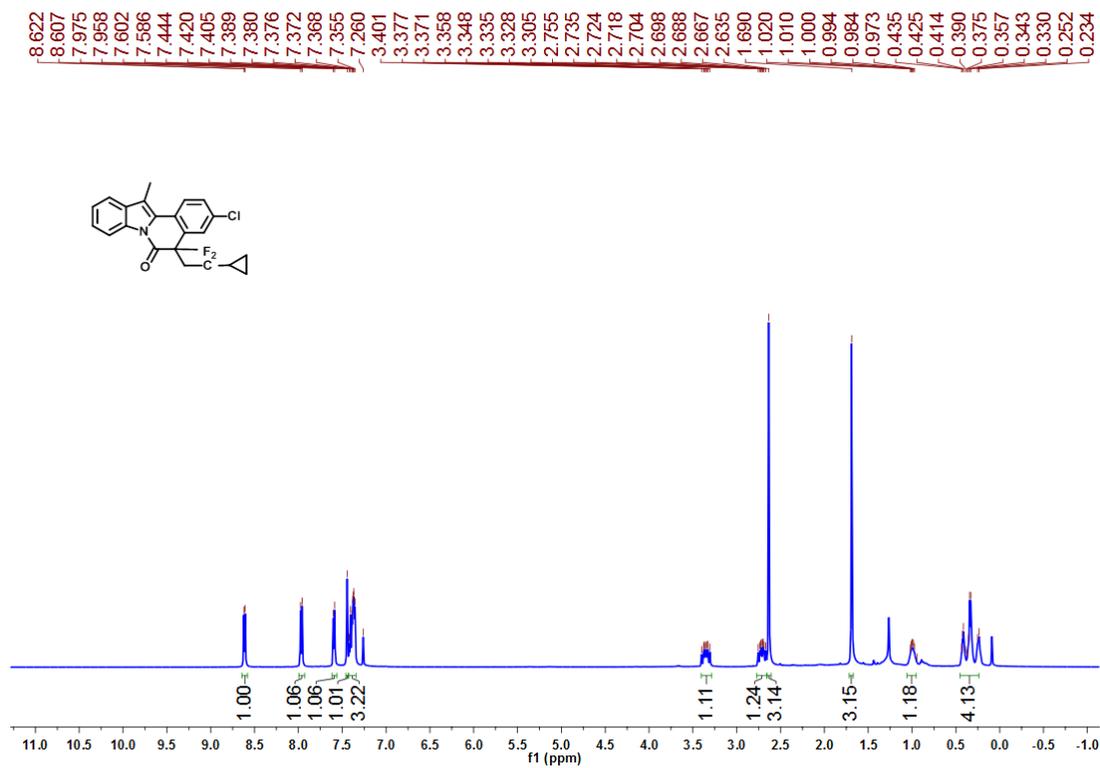
5h- ^{13}C { ^1H } NMR (125 MHz, CDCl_3)



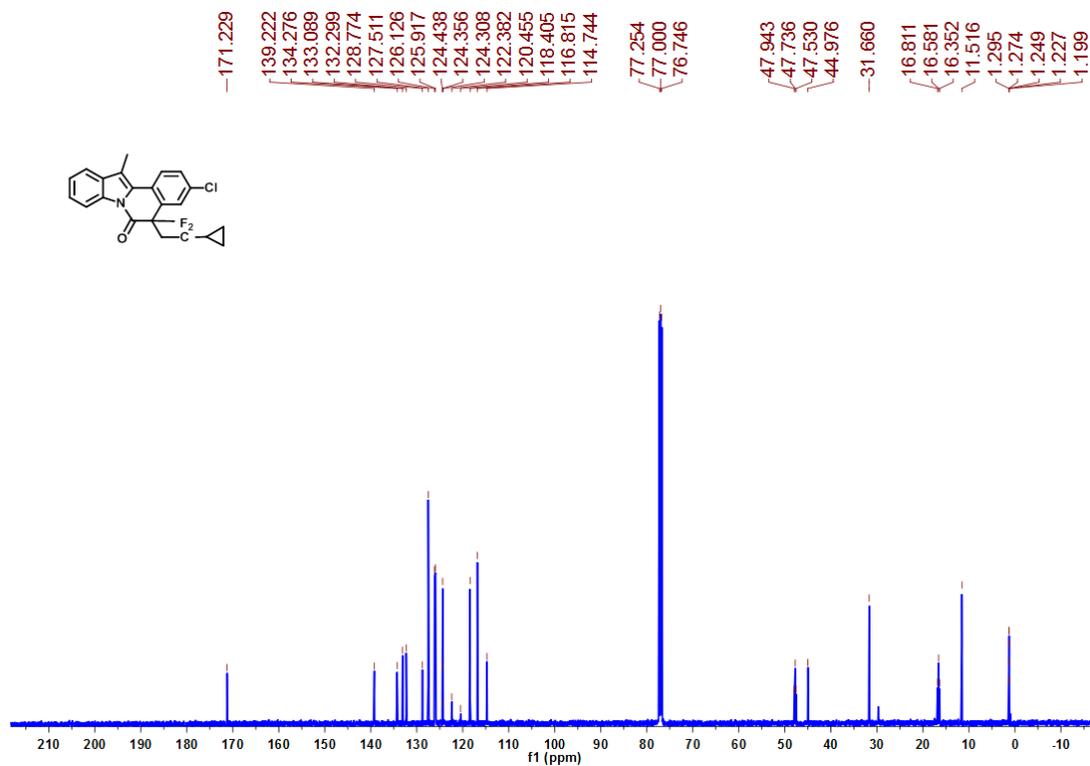
5h-¹⁹F NMR (471 MHz, CDCl₃)



5i-¹H NMR (500 MHz, CDCl₃)



5i-¹³C{¹H} NMR (125 MHz, CDCl₃)



5i-¹⁹F NMR (471 MHz, CDCl₃)

