

# Synthesis of methanesulfones-containing tetrasubstituted carbon stereocenters

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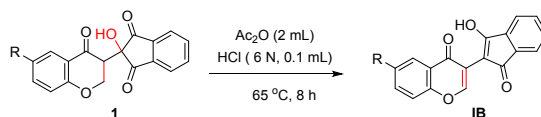
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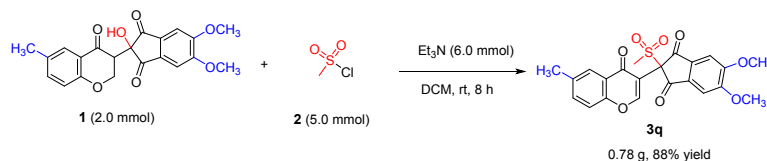
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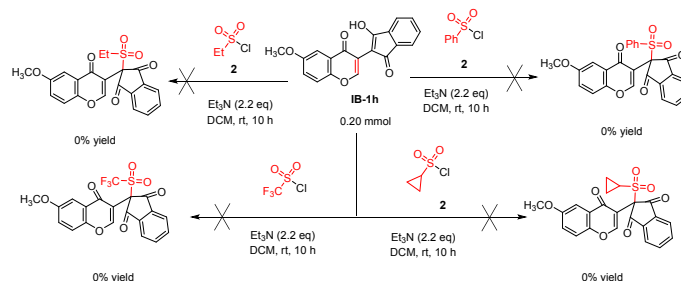
A solution of substrate **1** (0.20 mmol) in Ac<sub>2</sub>O (2.0 mL) was added HCl (6 N, 0.1 mL), and then stirred at 65 °C for 8 h. After completion of the reaction, as indicated by TLC, the removal of solvent and purification by flash column chromatography (hexane/EtOAc = 5:1~3:1) was carried out to furnish the indanedione-chromanone synthon **1B** as a red solid.

### 5. Gram scale synthesis of the product **3q**

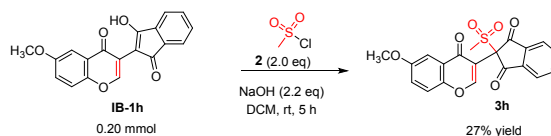


Compound **1** (2.0 mmol) and Et<sub>3</sub>N (6.0 mmol) were dissolved in DCM (15 mL). MsCl (5.0 mmol) was added to this solution at room temperature, and the mixture was stirred for 8 h. After the removal of solvent, purification by flash column chromatography (hexane/ethyl acetate = 8:1~5:1) was carried out to give product **3q** as a light yellow solid (0.78 g, 88% yield).

### 6. Scheme S1: control experiments



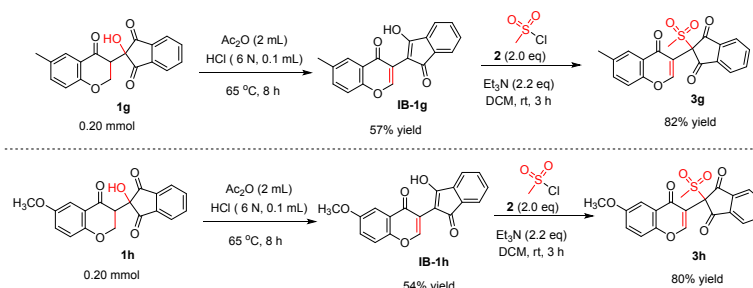
Compound **1B-1h** (0.20 mmol) and Et<sub>3</sub>N (0.44 mmol) was dissolved in DCM (1.5 mL). compound **2** (0.40 mmol) was added to this solution at room temperature, and the mixture was stirred for 10 h, however, the expected corresponding sulfone **3** was not observed with intractable product mixtures (0% yield).



Compound **1B-1h** (0.20 mmol) and NaOH (0.44 mmol) was dissolved in DCM (1.5 mL). compound **2** (0.40 mmol) was added to this solution at room temperature, and the mixture was

stirred for 5 h. After the removal of solvent, purification by flash column chromatography (hexane/ethyl acetate = 8:1~5:1) was carried out to give product **3h** as a light yellow solid (27% yield).

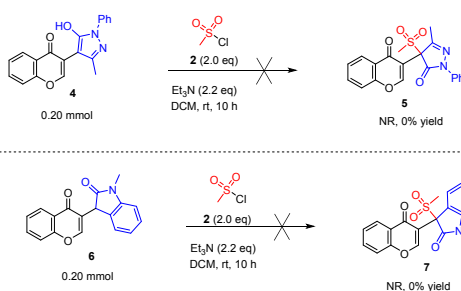
## 7. Scheme S2: control experiments



Compound **1** (0.20 mmol) was dissolved in Ac<sub>2</sub>O (2 mL). HCl (6 N, 0.1 mL) was added to this solution at 65 °C, and the mixture was stirred for 8 h. After the removal of solvent, purification by flash column chromatography (hexane/ethyl acetate = 8:1~5:1) was carried out to give intermediate **IB** as a red solid.

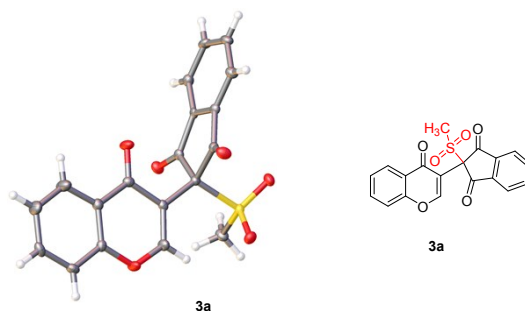
Intermediate **IB** (0.2 mmol) and Et<sub>3</sub>N (4.4 mmol) were dissolved in DCM (1.5 mL). MsCl (0.40 mmol) was added to this solution at room temperature, and the mixture was stirred for 3 h. After the removal of solvent, purification by flash column chromatography (hexane/ethyl acetate = 6:1~4:1) was carried out to give product **3** as a light yellow solid.

## 8. Scheme S3: other substrates in this transformation



Compound **4** or **6** (0.20 mmol) and Et<sub>3</sub>N (0.44 mmol) was dissolved in DCM (1.5 mL). compound **2** (0.40 mmol) was added to this solution at room temperature, and the mixture was stirred for 10 h, however, the expected corresponding sulfone **5** or **7** was not observed with recovery of starting material **4** or **6** (0% yield).

## 9. X-Ray Crystal Data for Compound 3a



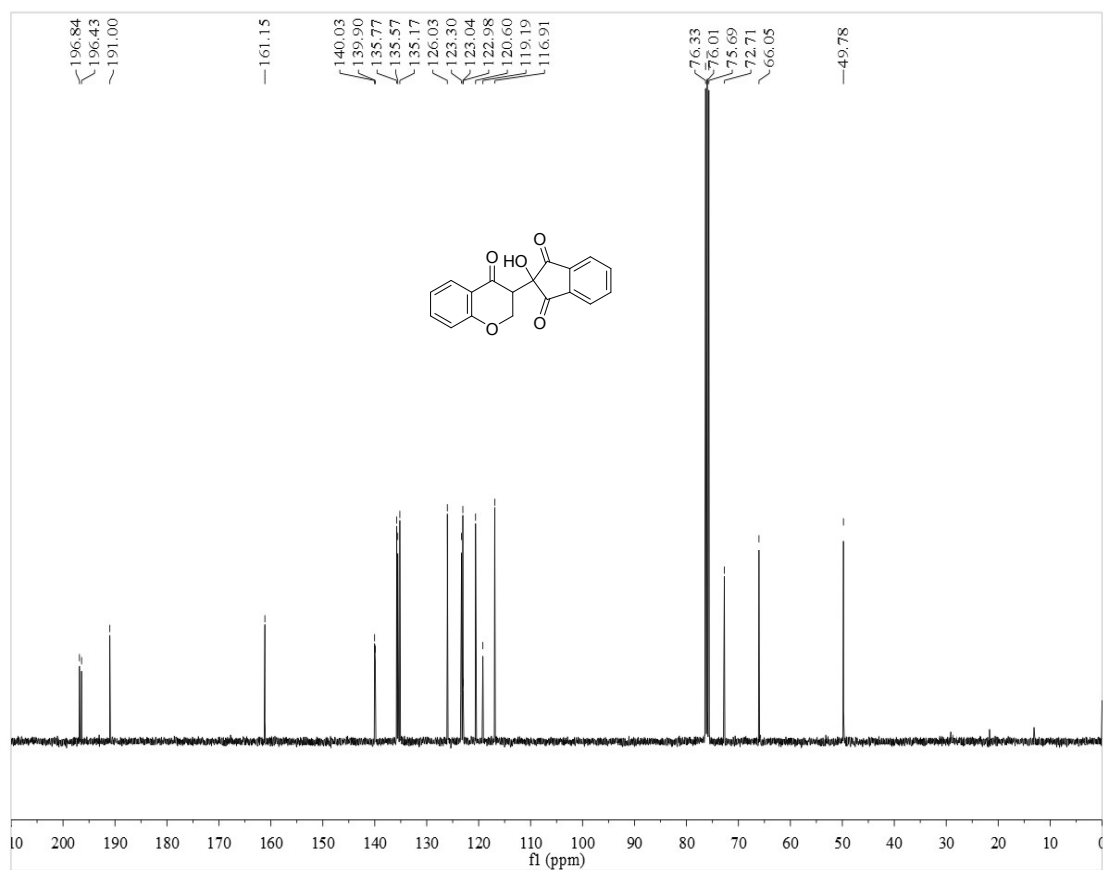
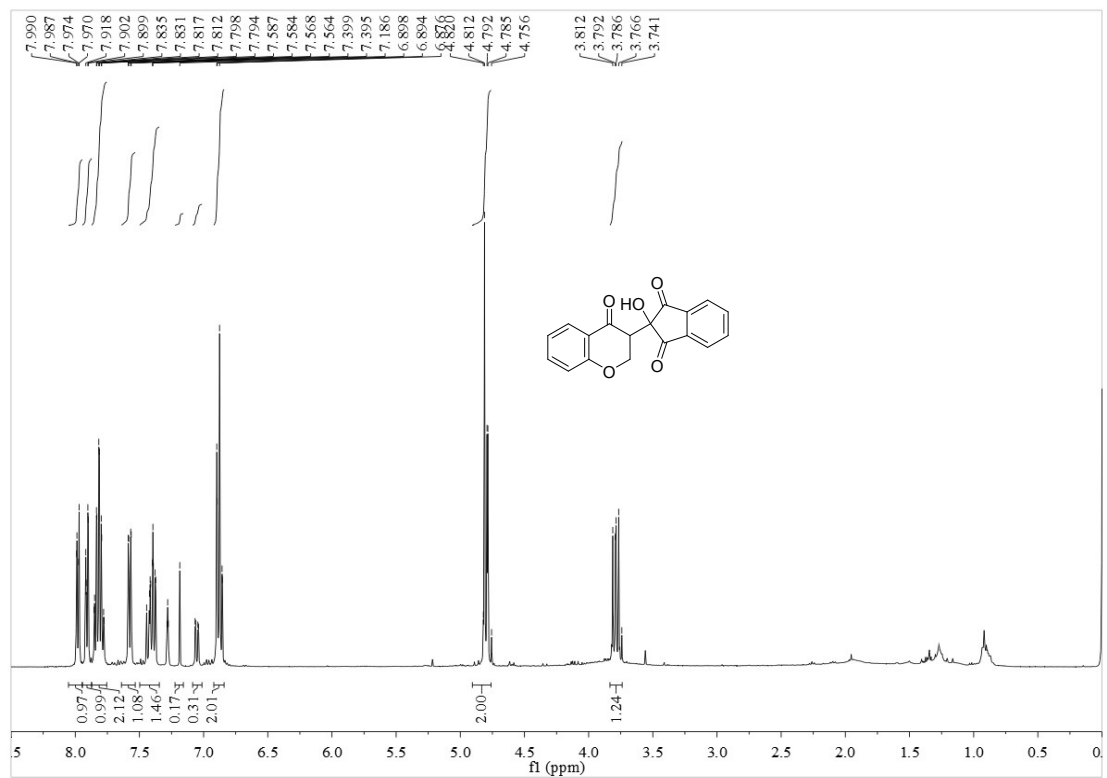
**Table S1 Crystal data and structure refinement for 3a**

Identification code	<b>3a</b>
Empirical formula	C <sub>19</sub> H <sub>12</sub> O <sub>6</sub> S
Formula weight	368.35
Temperature/K	100.00(10)
Crystal system	triclinic
Space group	P-1
a/Å, b/Å, c/Å	7.6249(5), 9.1227(5), 12.8047(9)
α/°, β/°, γ/°	85.841(5), 88.200(5), 81.018(5).
Volume/Å <sup>3</sup>	877.27(10)
Z	2
ρ <sub>calc</sub> /cm <sup>3</sup>	1.394
μ/mm <sup>-1</sup>	0.217
F(000)	380.0
Radiation	Mo Kα (λ = 0.71073)
Crystal size/mm <sup>3</sup>	0.14 × 0.13 × 0.12
2θ range for data collection/°	4.532 to 49.994
Index ranges	-9 ≤ h ≤ 9, -10 ≤ k ≤ 10, -12 ≤ l ≤ 15
Reflections collected	5655
Independent reflections	3074 [R <sub>int</sub> = 0.0247, R <sub>sigma</sub> = 0.0446]
Data/restraints/parameters	3074/0/236
Goodness-of-fit on F <sup>2</sup>	1.097
Final R indexes [I >= 2σ (I)]	R <sub>1</sub> = 0.0470, wR <sub>2</sub> = 0.1165
Final R indexes [all data]	R <sub>1</sub> = 0.0532, wR <sub>2</sub> = 0.1205
Largest diff. peak/hole / e Å <sup>-3</sup>	0.41/-0.49

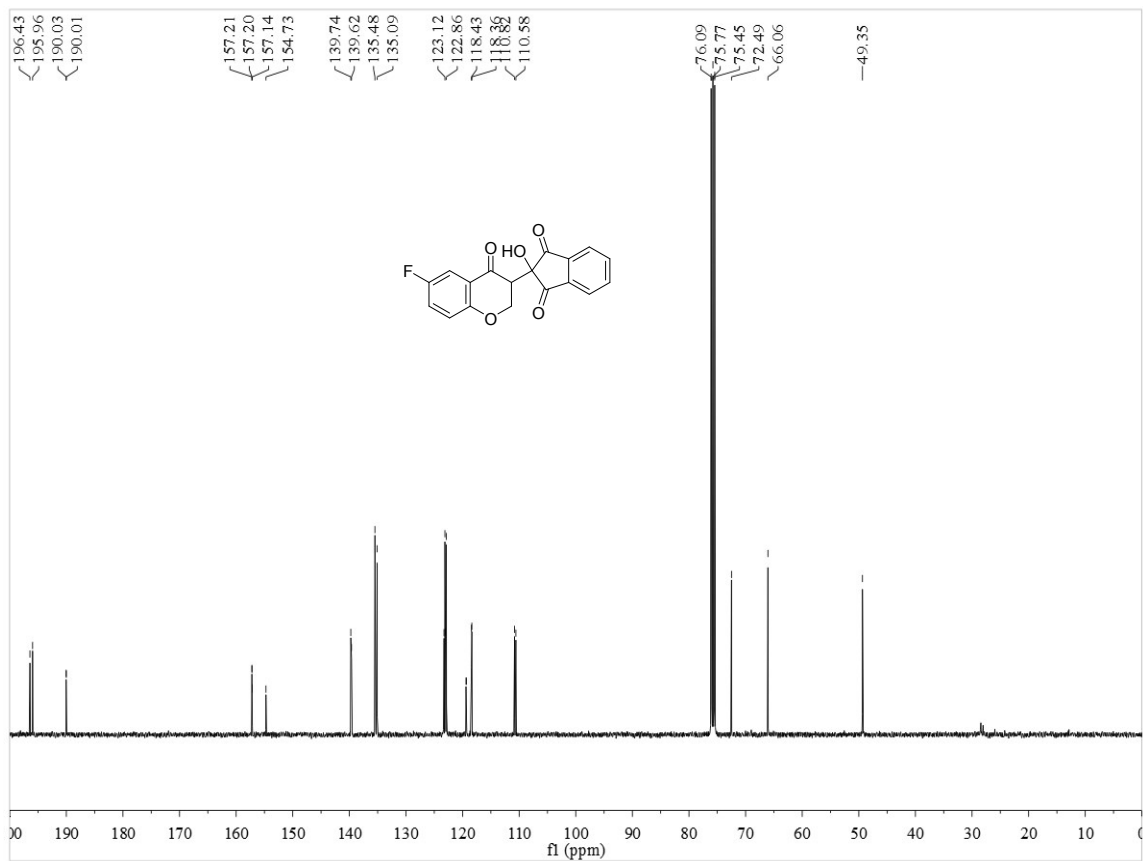
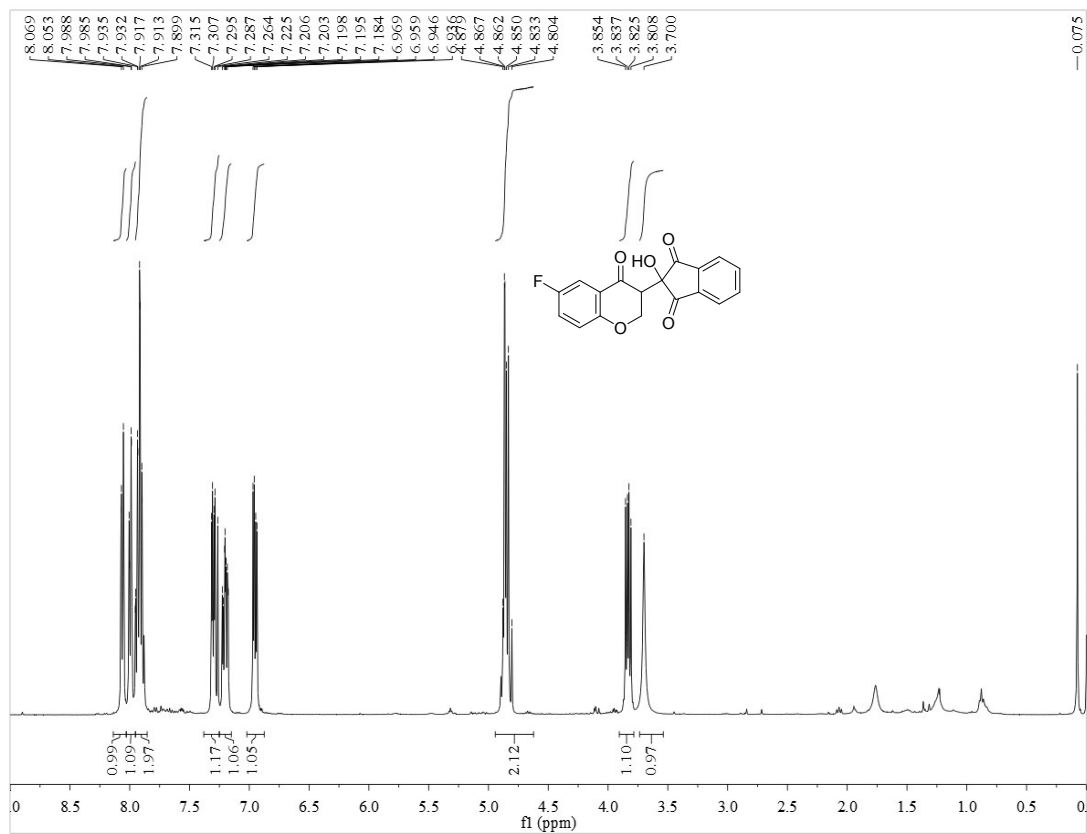
Crystal data for **3a**: (*M* = 368.35 g/mol): triclinic, space group P-1 (no. 2), *a* = 7.6249(5) Å, *b* = 9.1227(5) Å, *c* = 12.8047(9) Å, α = 85.841(5)°, β = 88.200(5)°, γ = 81.018(5)°, *V* = 877.27(10) Å<sup>3</sup>, *Z* = 2, *T* = 100.00(10) K, μ(Mo Kα) = 0.217 mm<sup>-1</sup>, *D*<sub>calc</sub> = 1.394 g/cm<sup>3</sup>, 5655 reflections measured (4.532° ≤ 2θ ≤ 49.994°), 3074 unique (*R*<sub>int</sub> = 0.0247, *R*<sub>sigma</sub> = 0.0446) which were used in all calculations. The final *R*<sub>1</sub> was 0.0470 (*I* > 2σ(*I*)) and *wR*<sub>2</sub> was 0.1205 (all data).

### 10. The Copies of $^1\text{H}$ NMR, $^{13}\text{C}$ NMR and $^{19}\text{F}$ NMR Spectra for Compounds 1 and 3

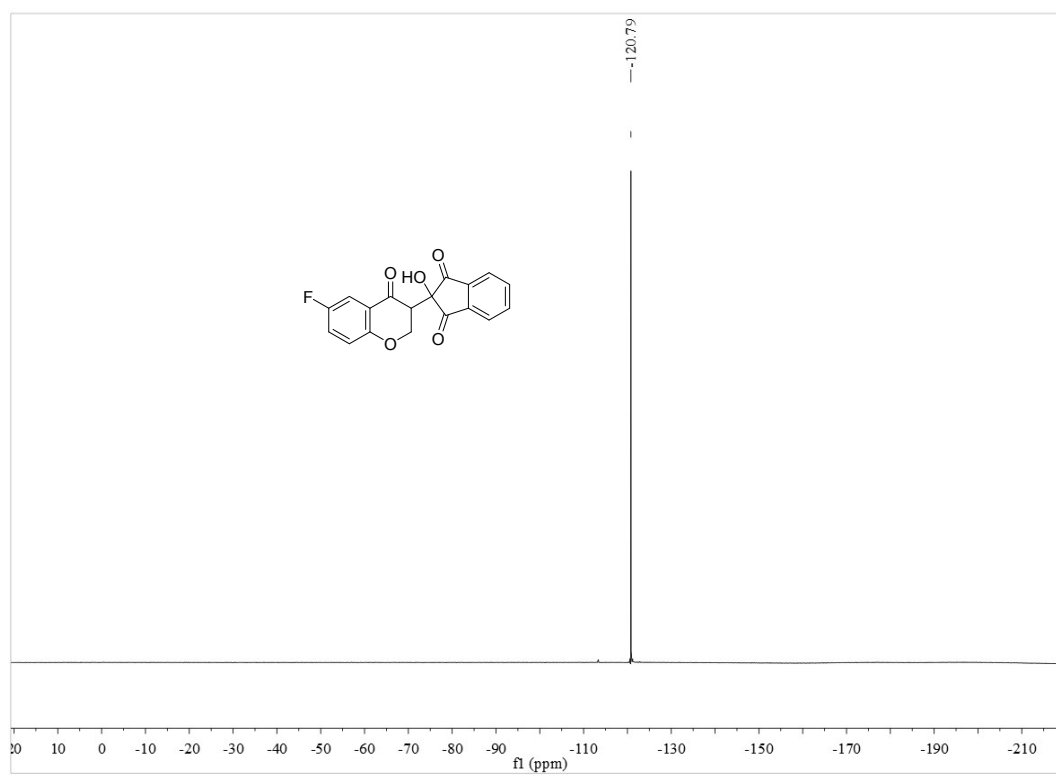
#### $^1\text{H}$ and $^{13}\text{C}$ NMR of 1a



# <sup>1</sup>H and <sup>13</sup>C NMR of 1b

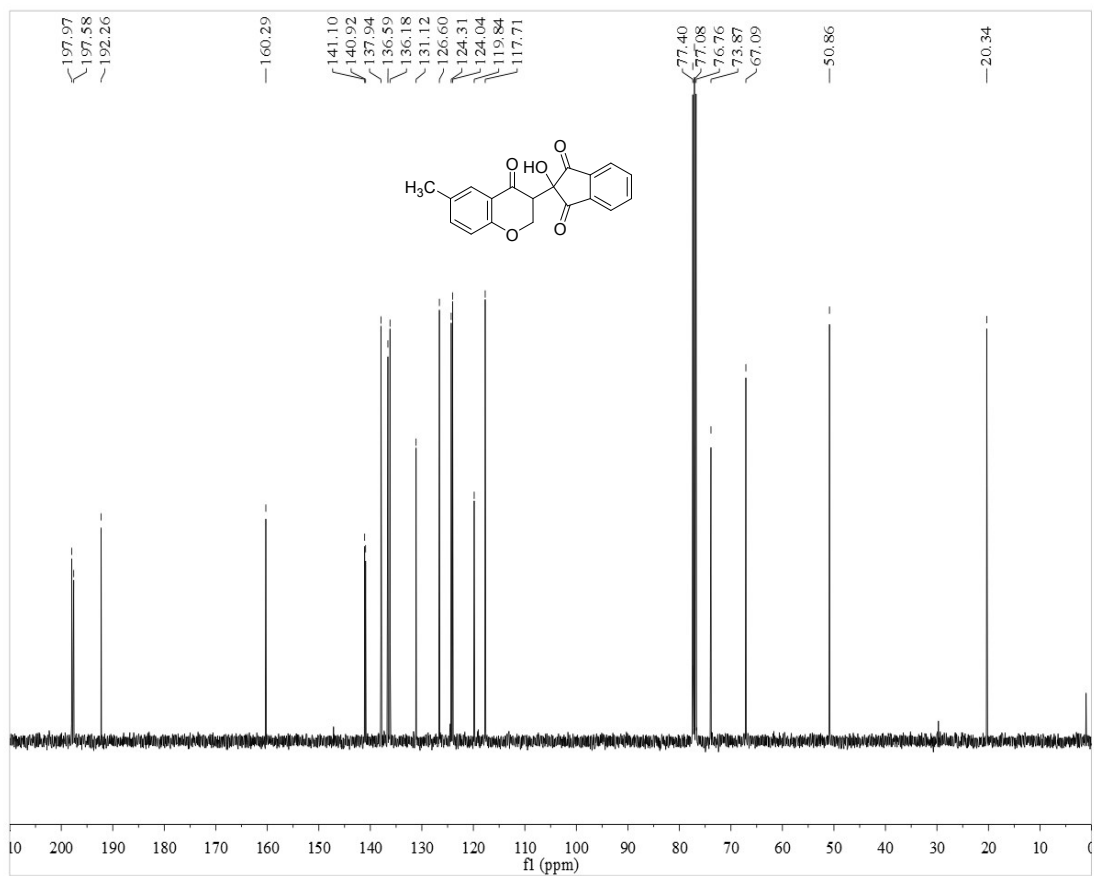
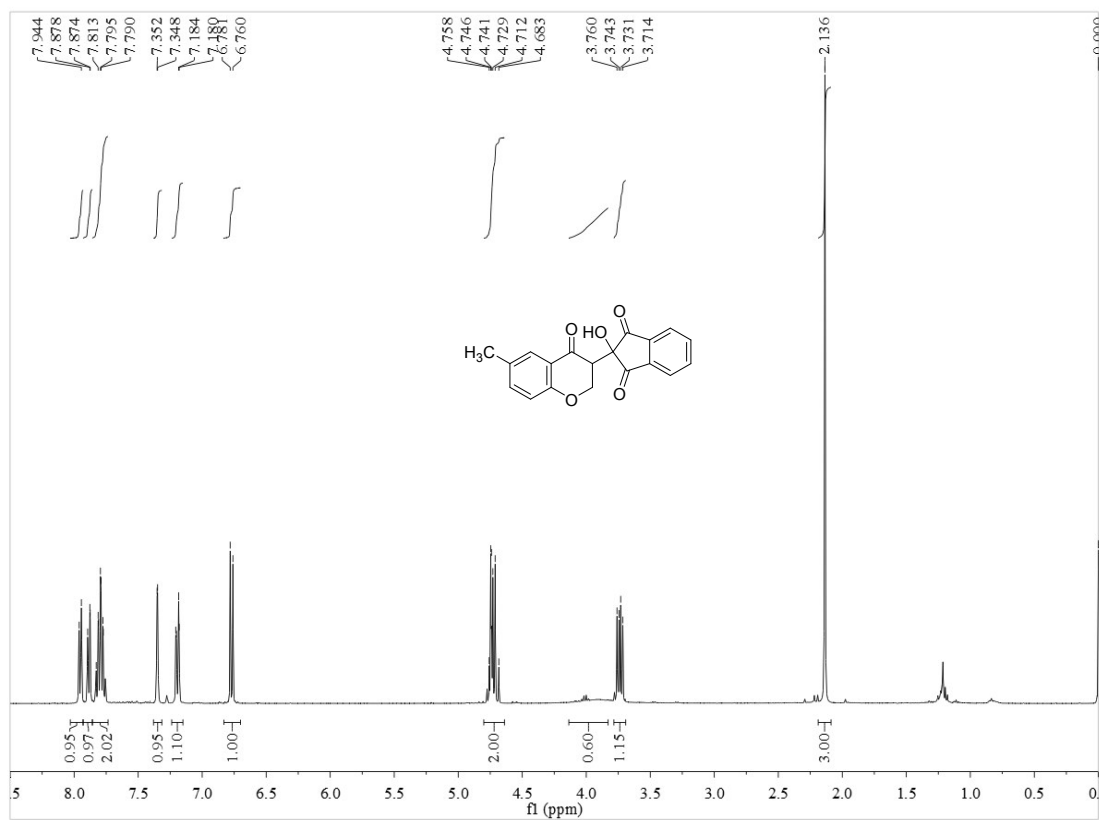


# <sup>19</sup>F NMR of 1b

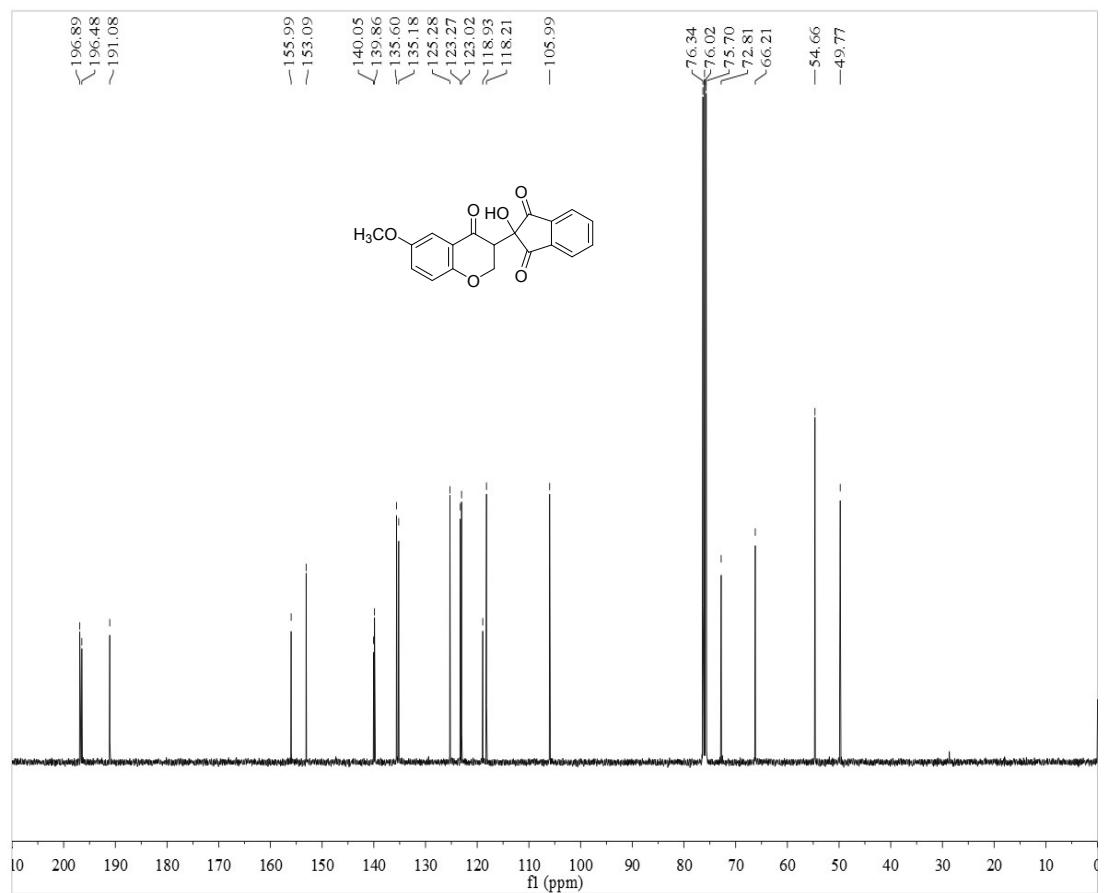
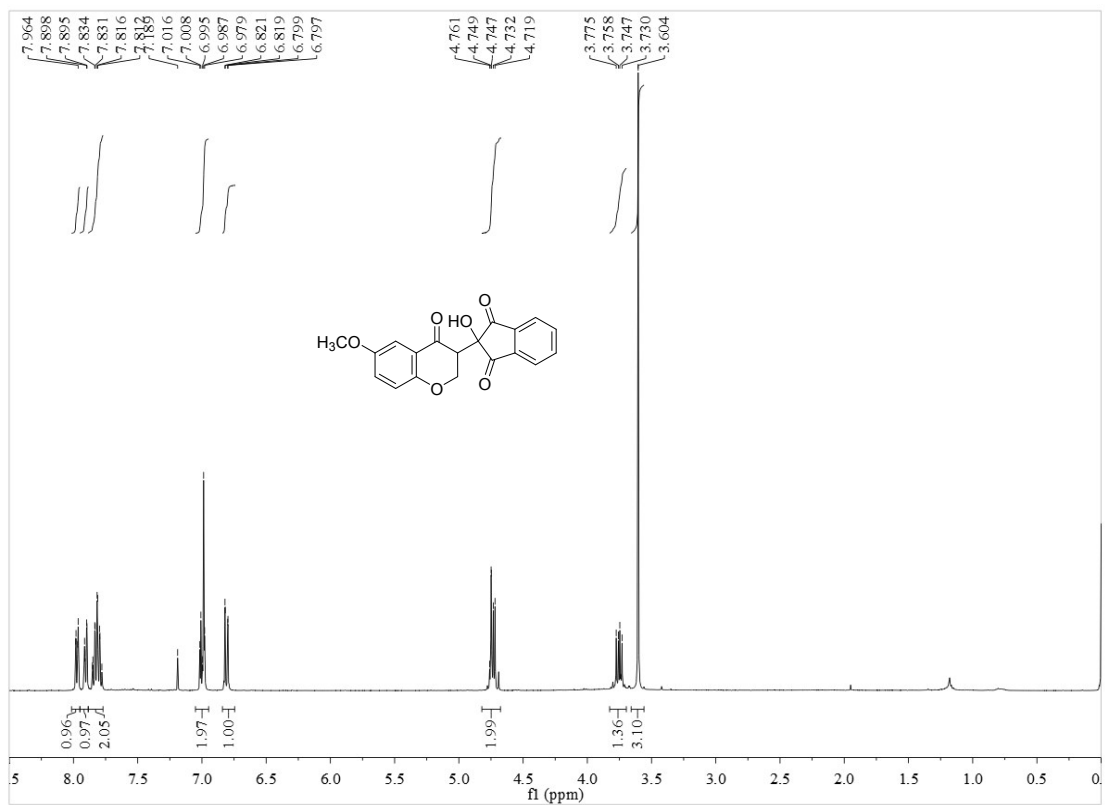




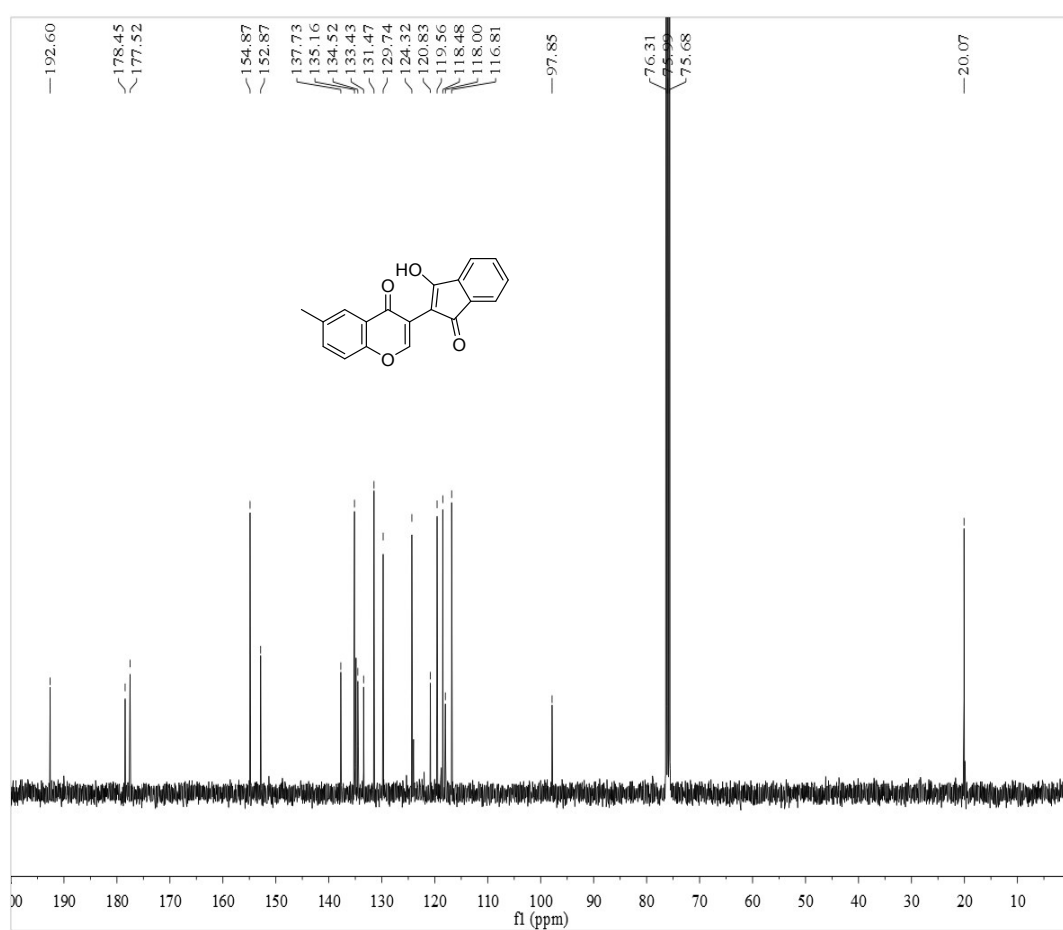
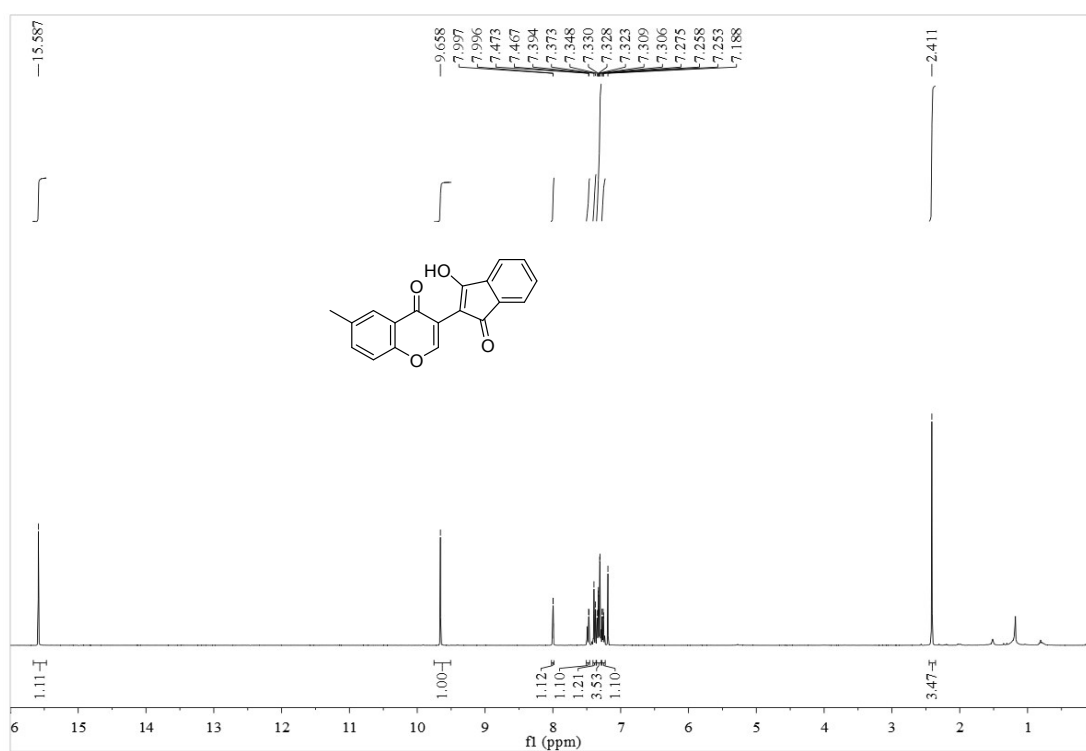
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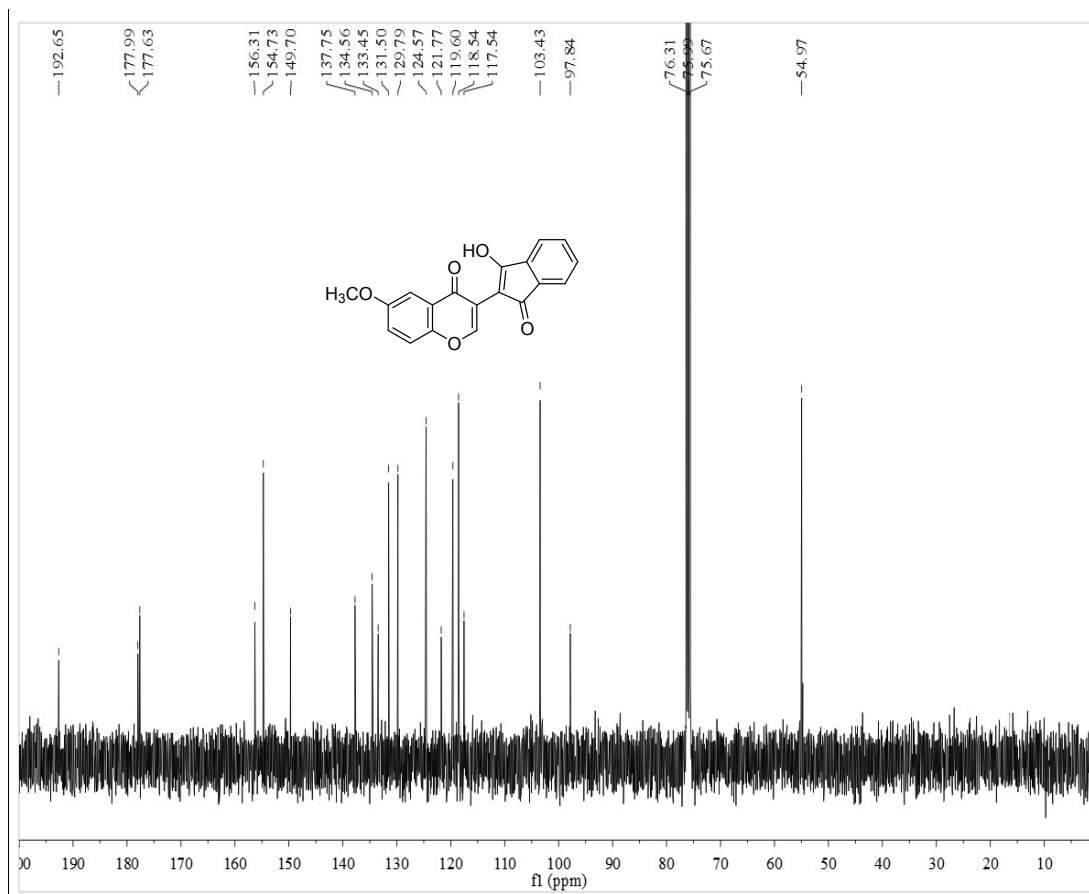
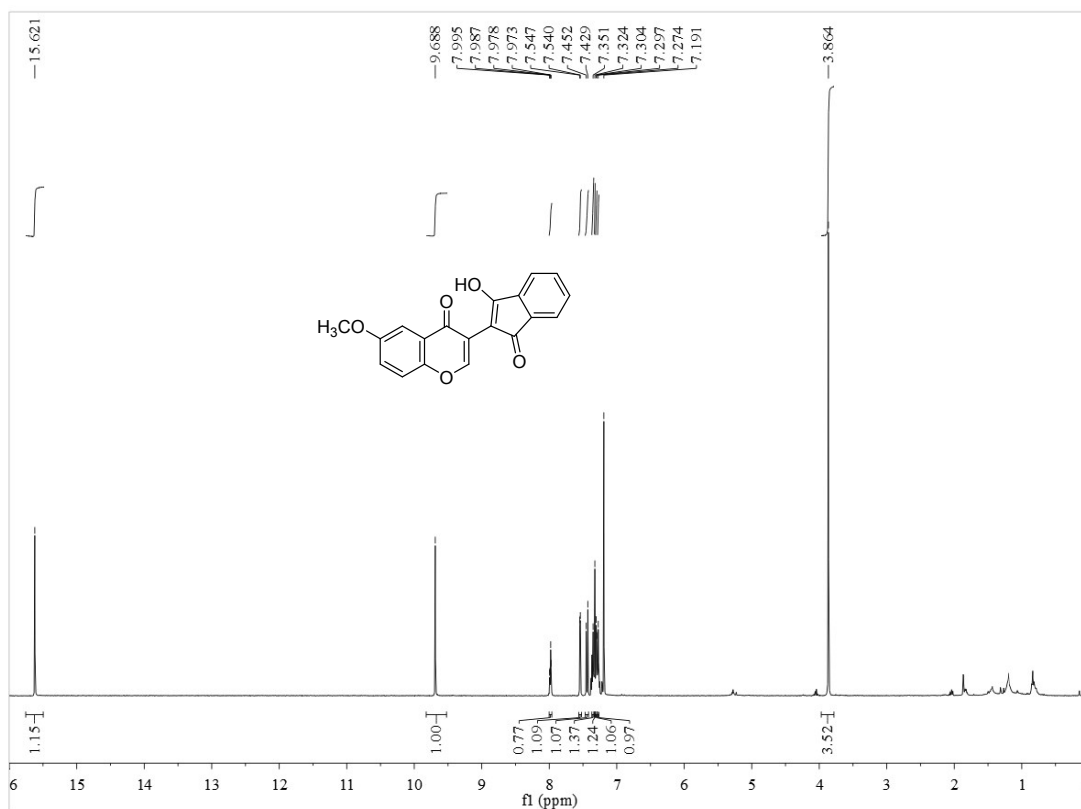
# <sup>1</sup>H and <sup>13</sup>C NMR of 1d



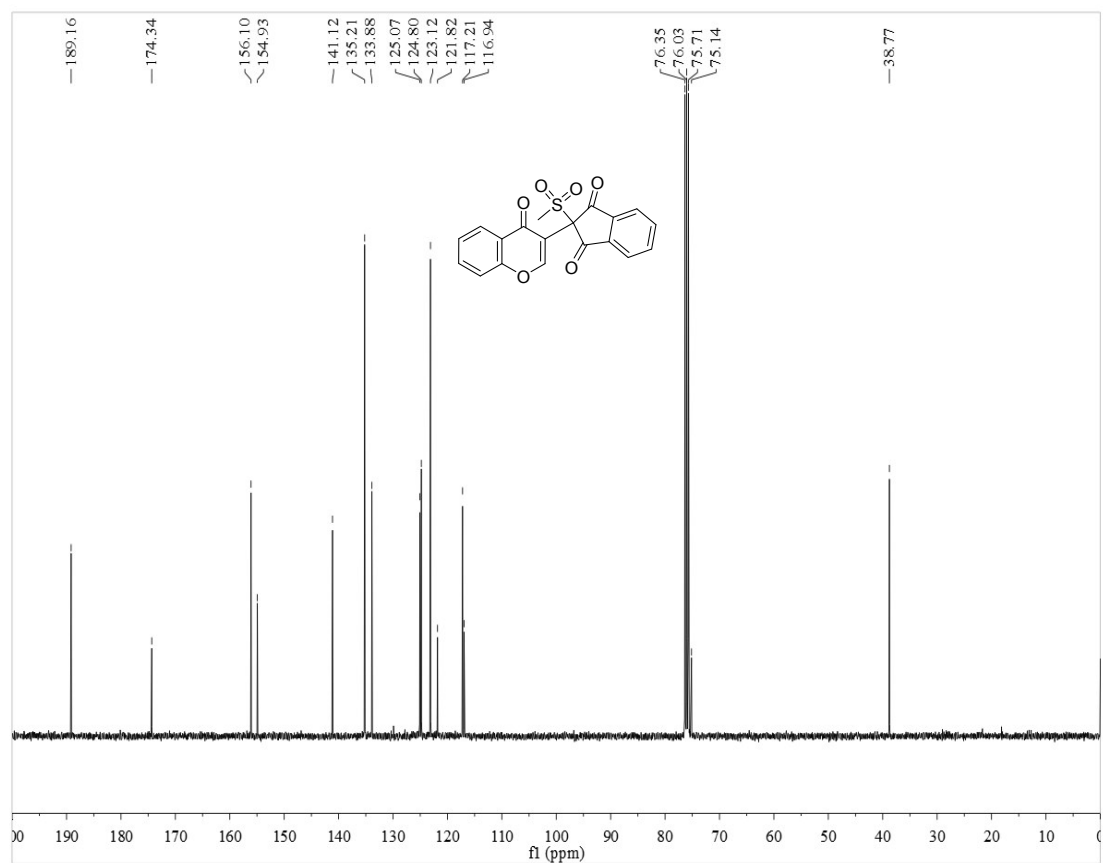
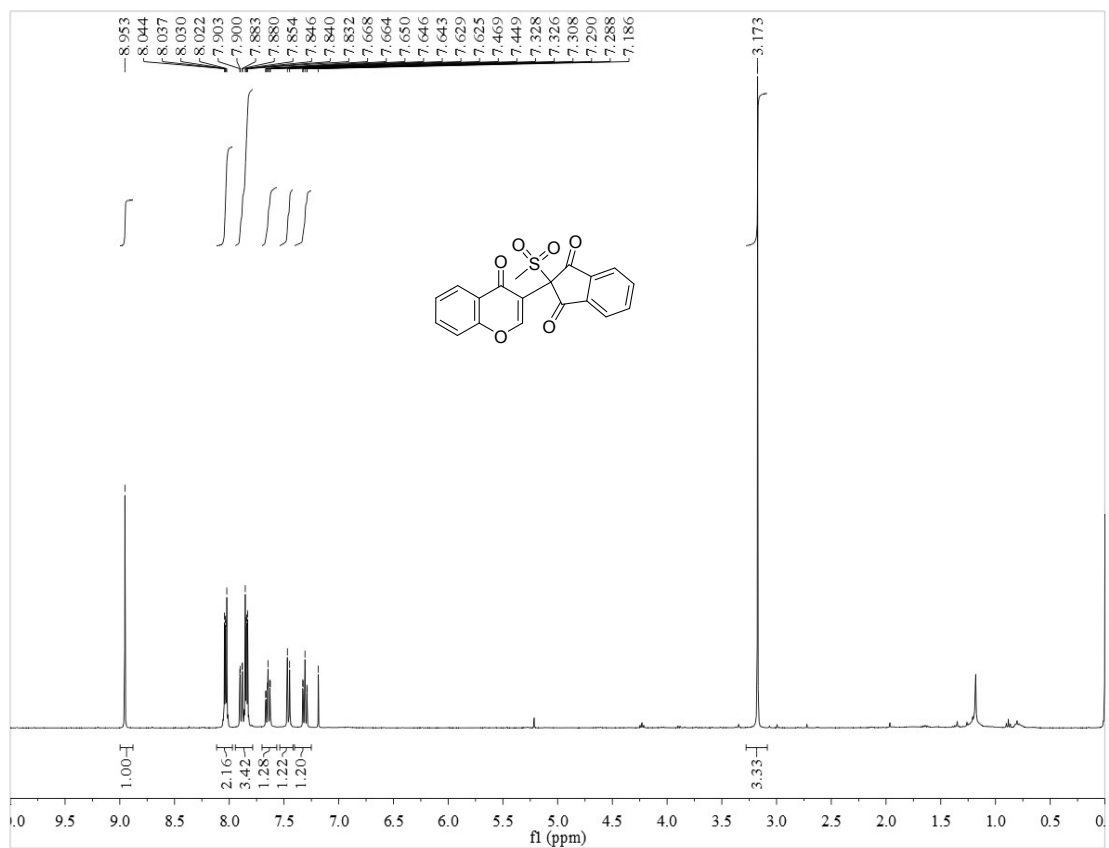
# <sup>1</sup>H and <sup>13</sup>C NMR of 1B-1g



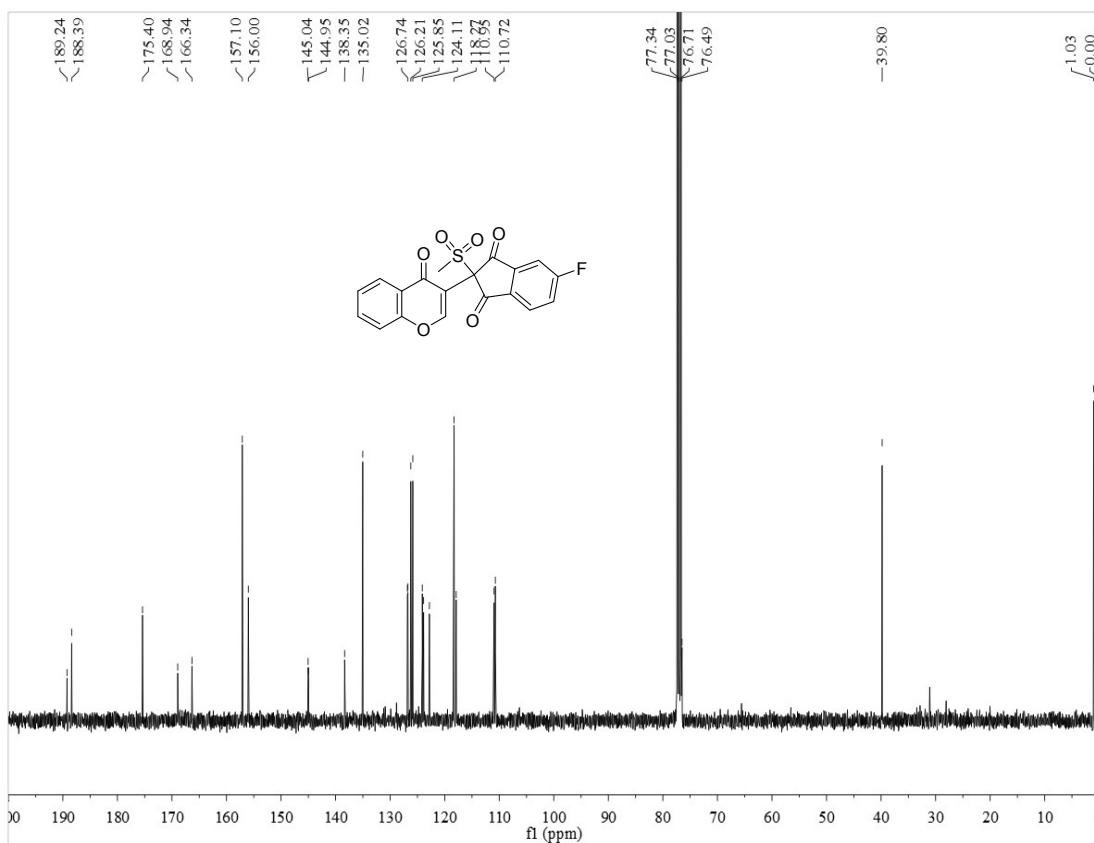
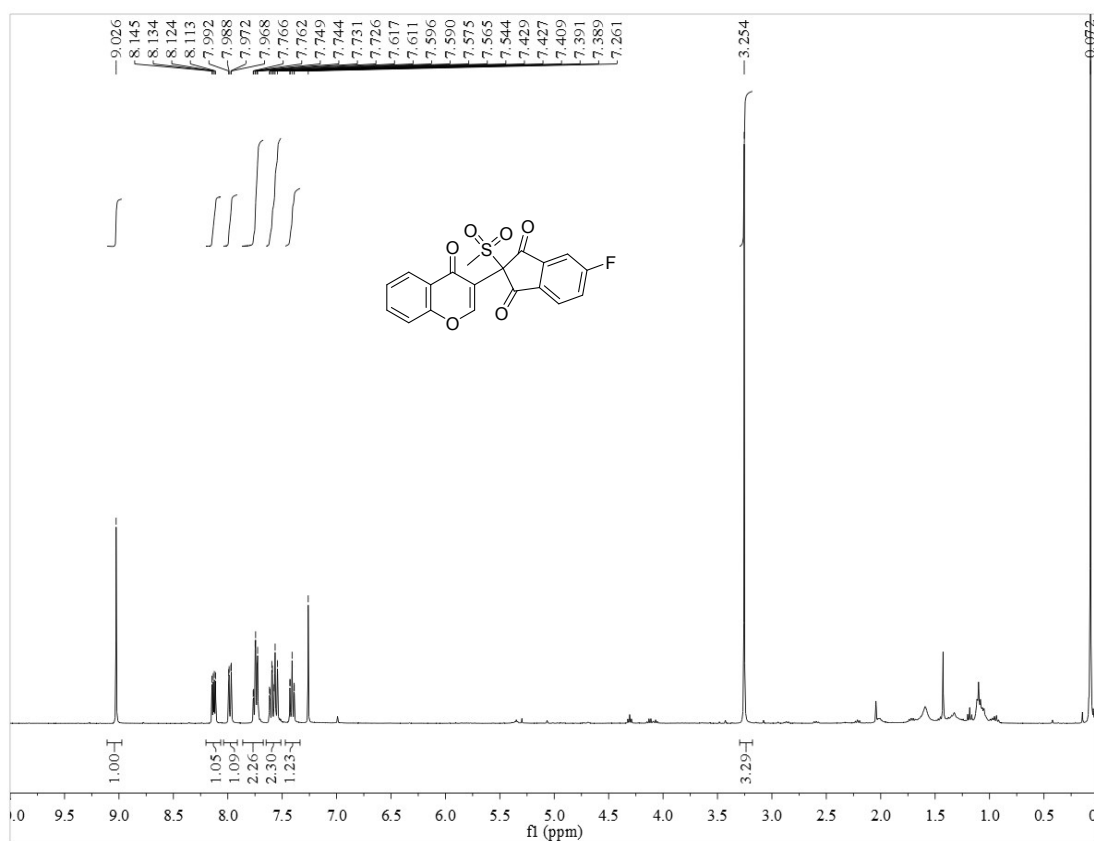
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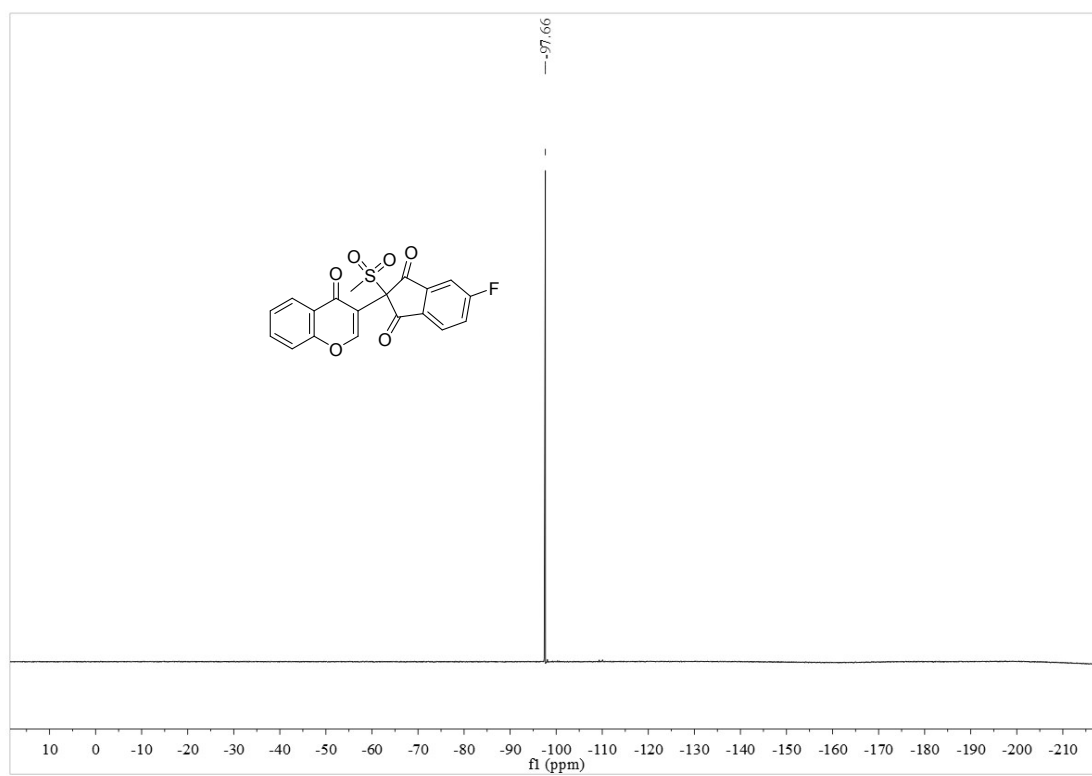
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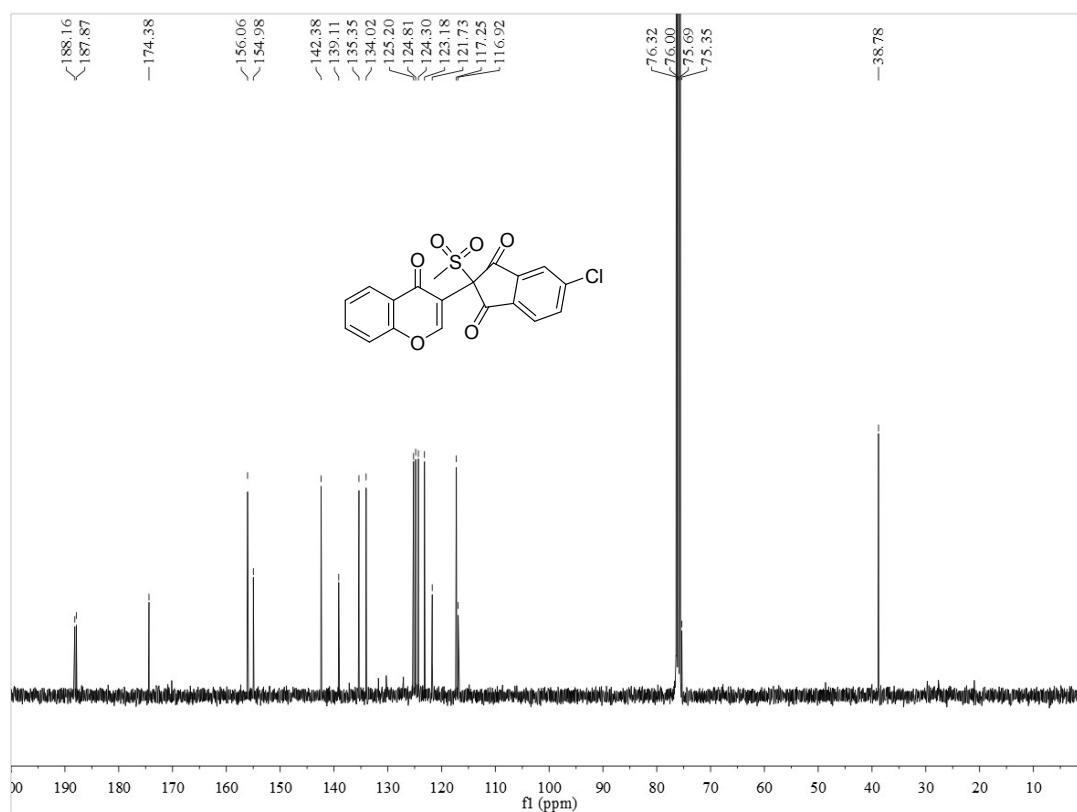
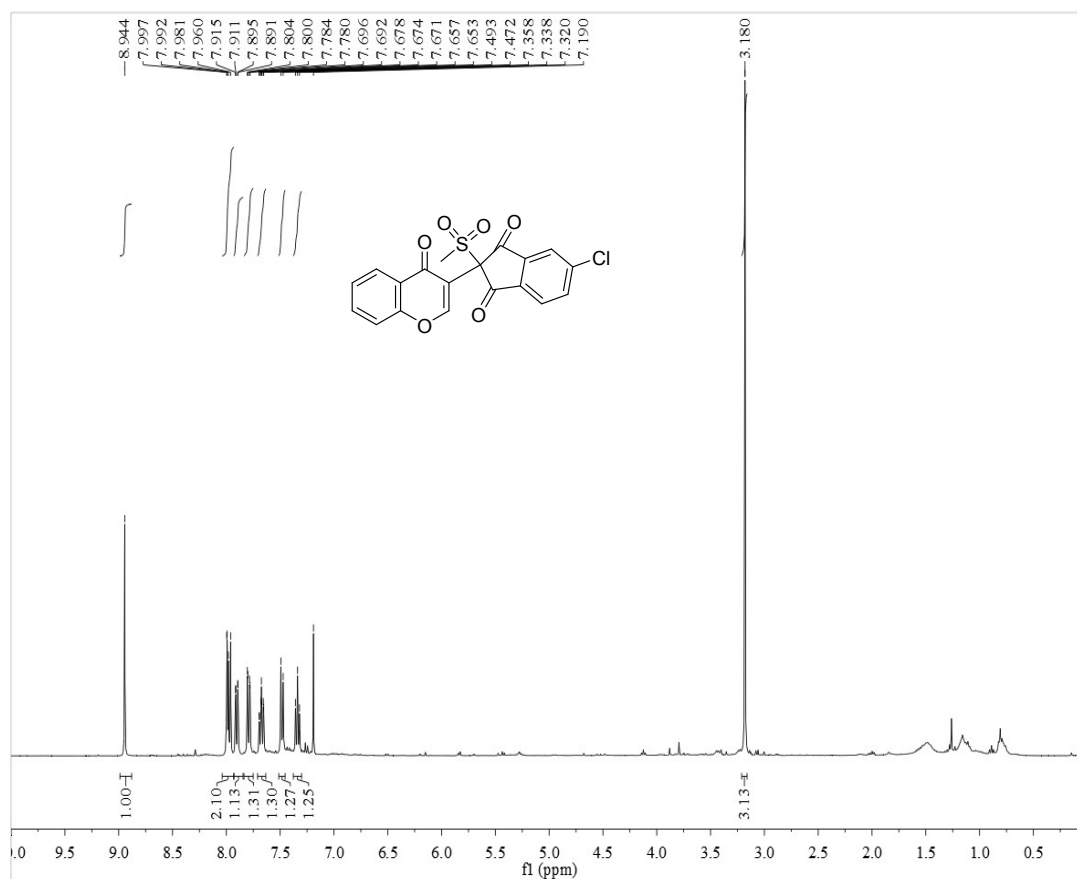
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### <sup>19</sup>F NMR of 3b

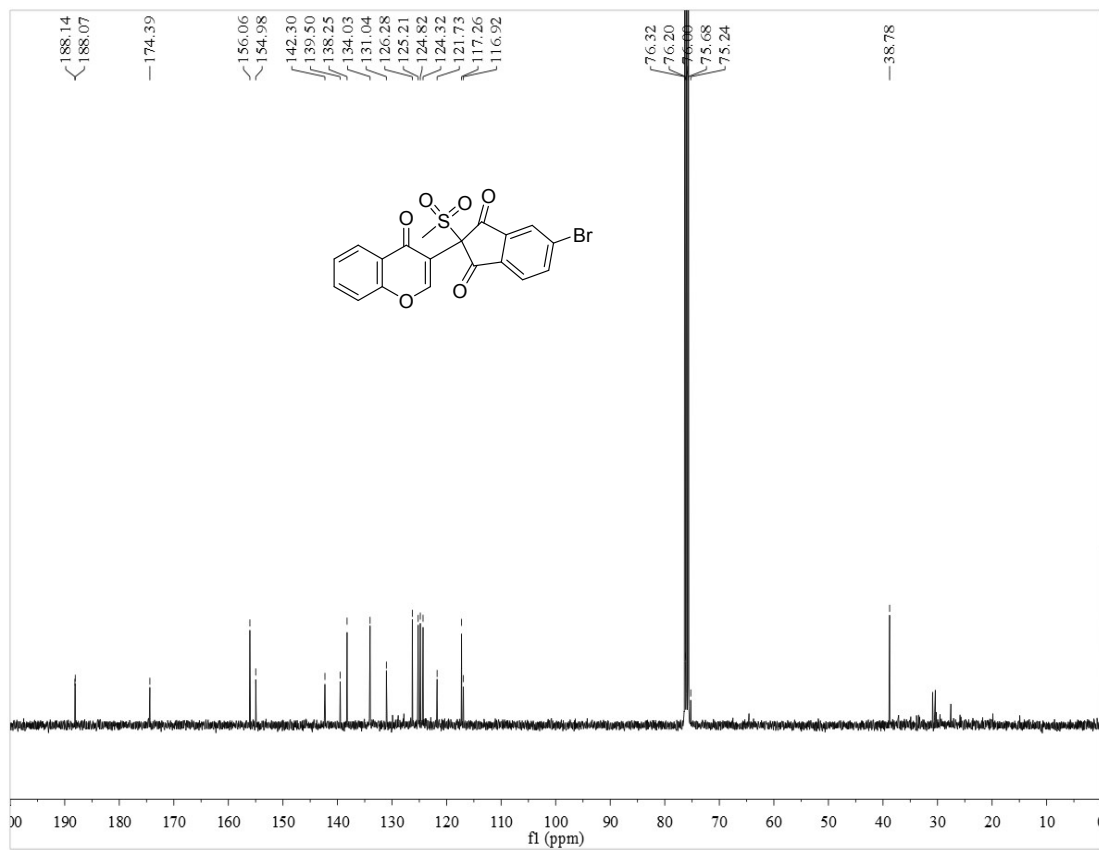
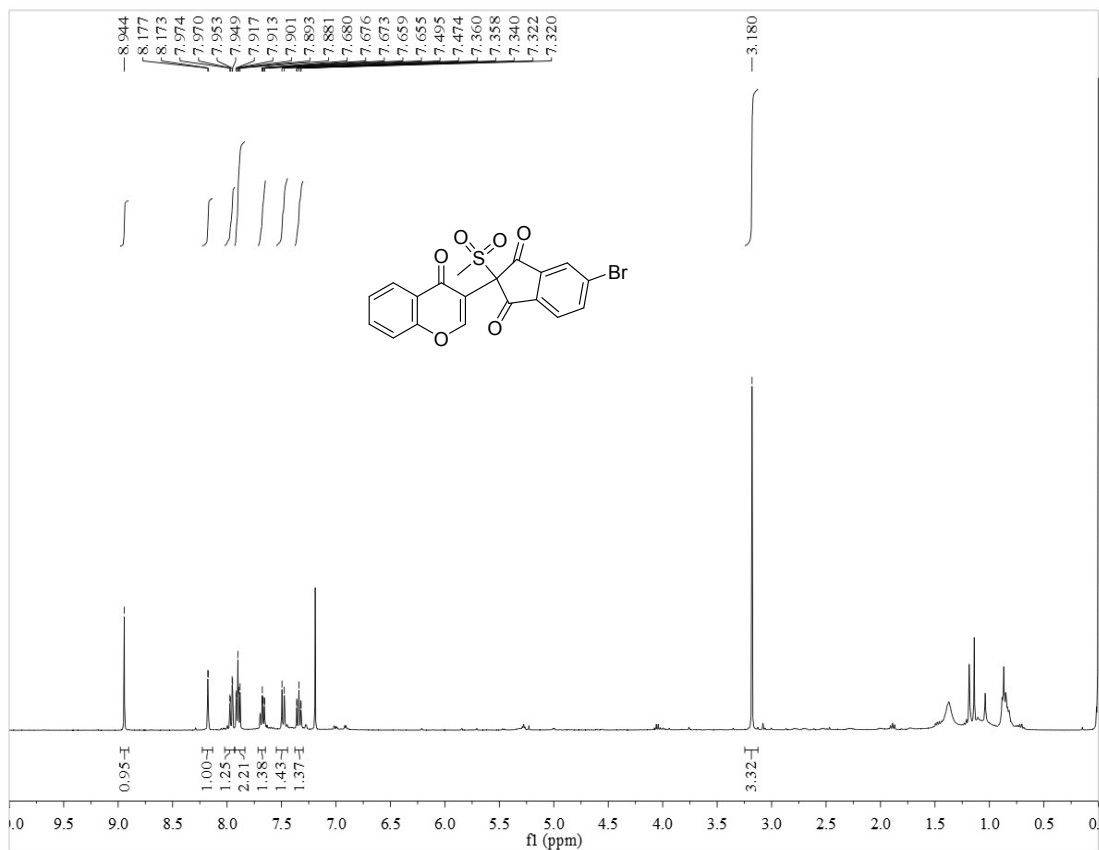


# <sup>1</sup>H and <sup>13</sup>C NMR of 3c

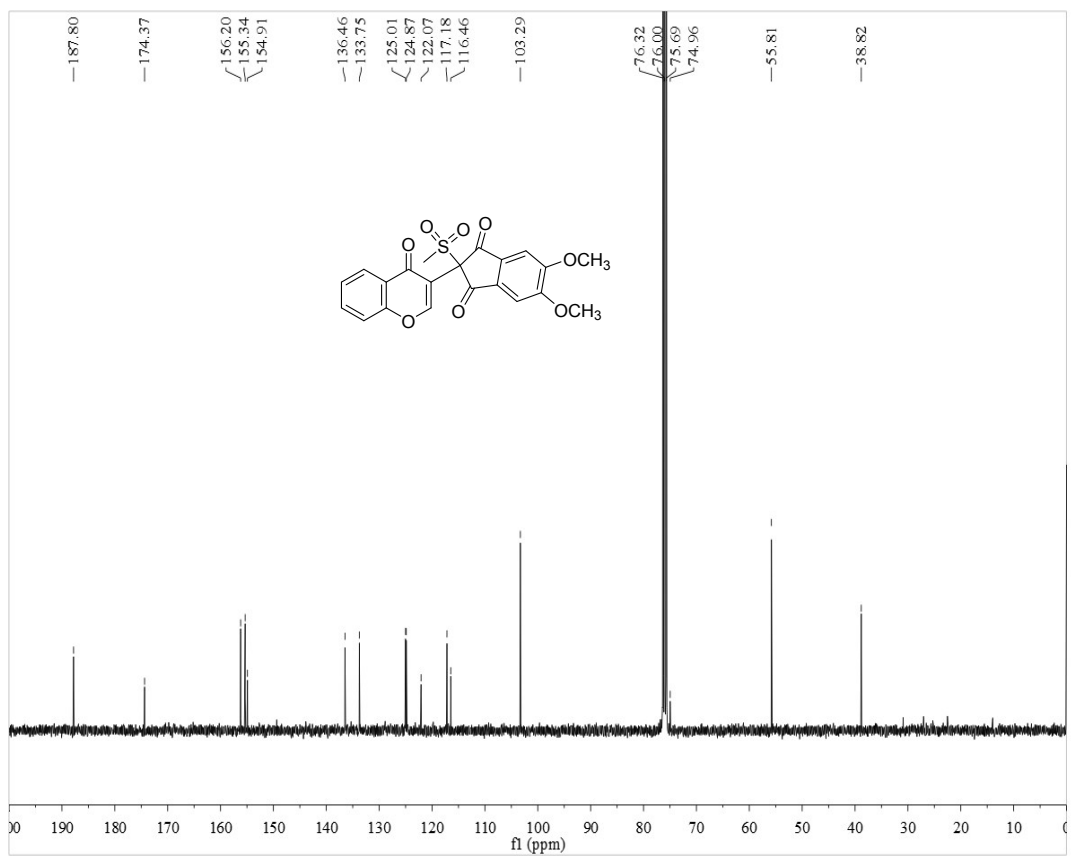
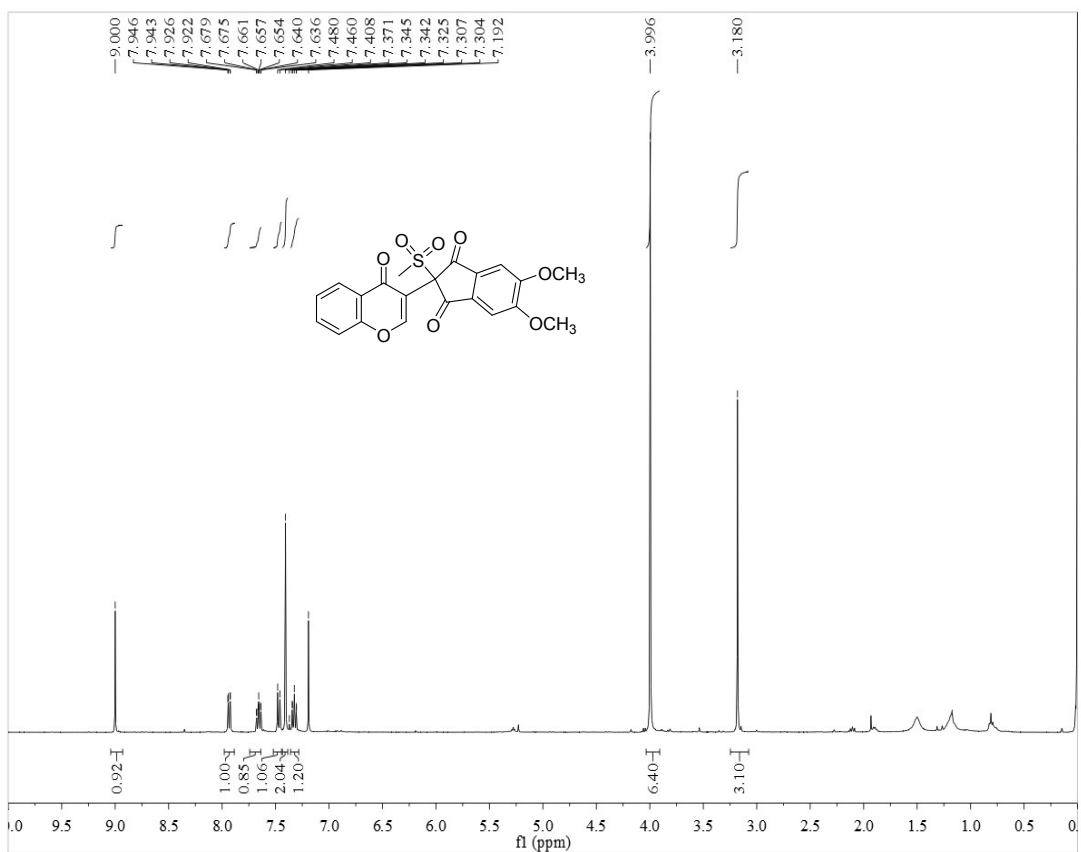




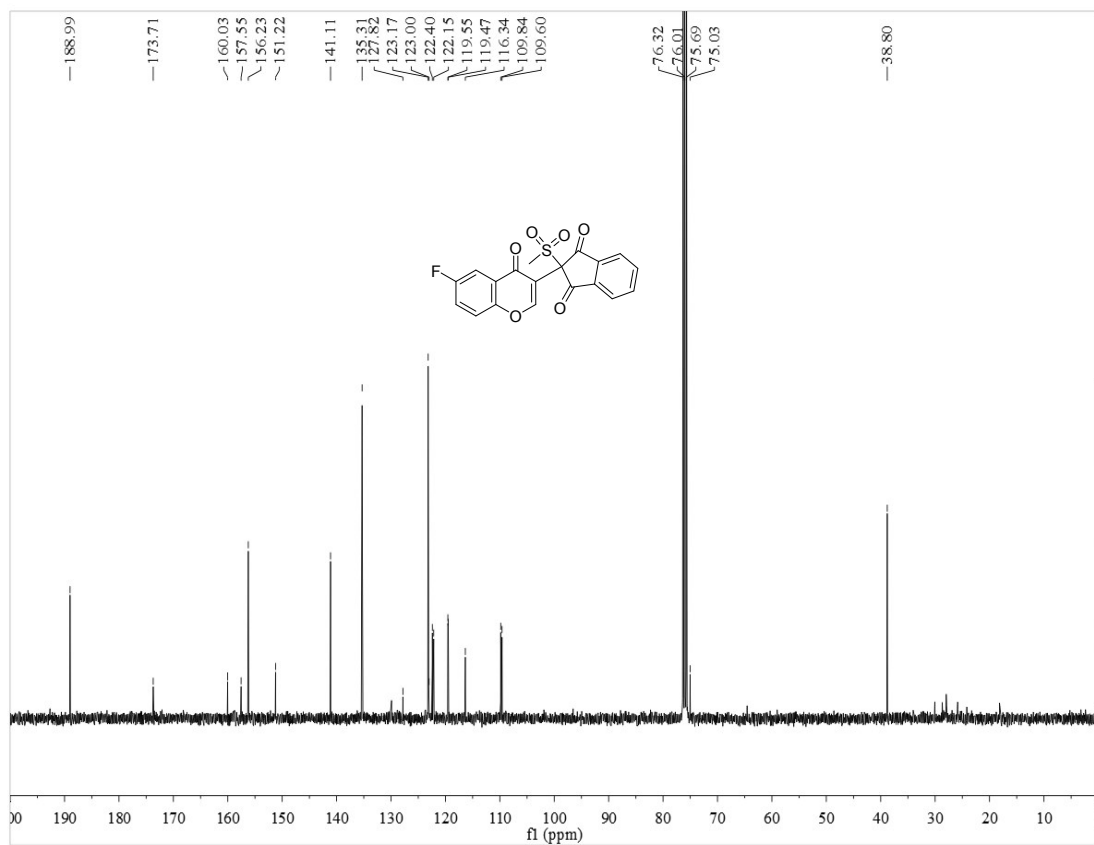
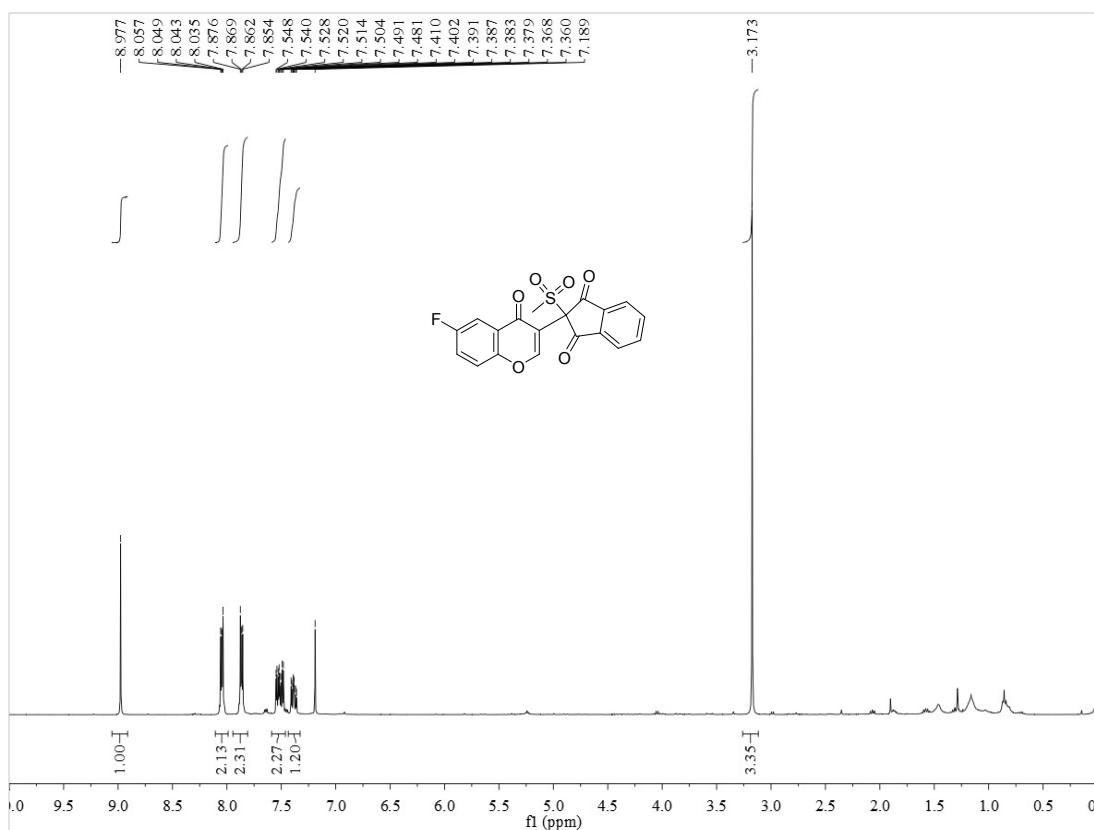
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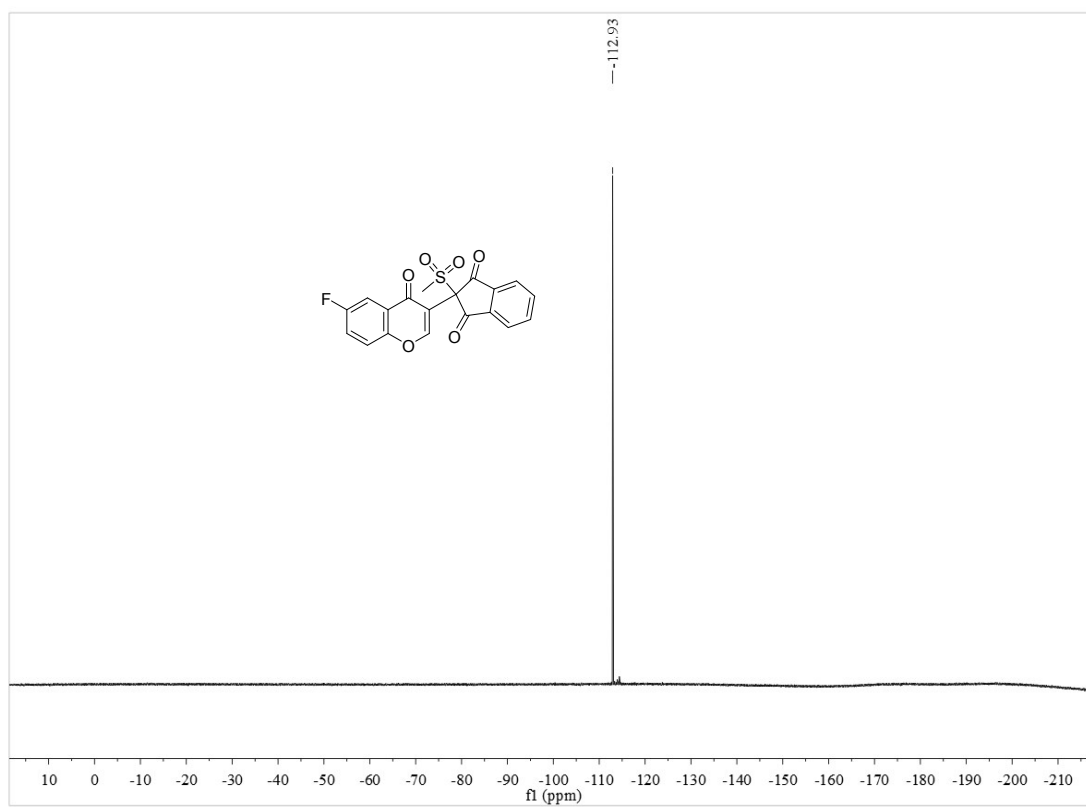
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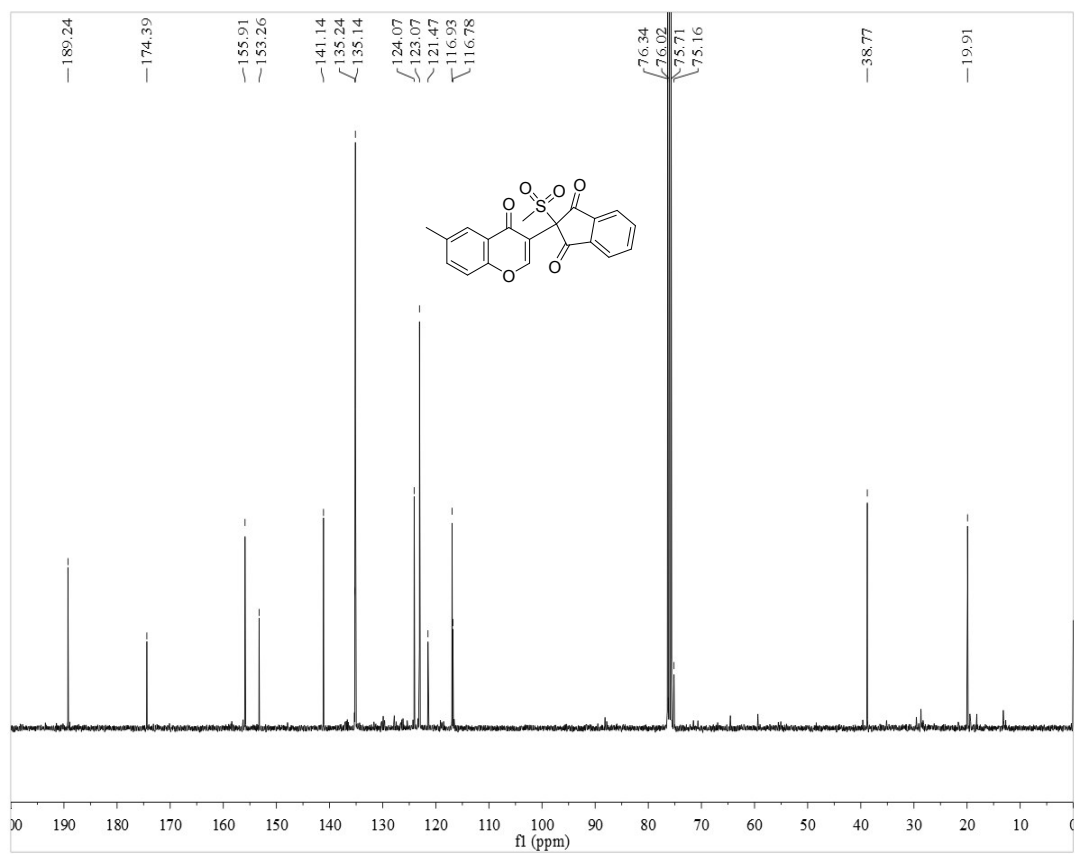
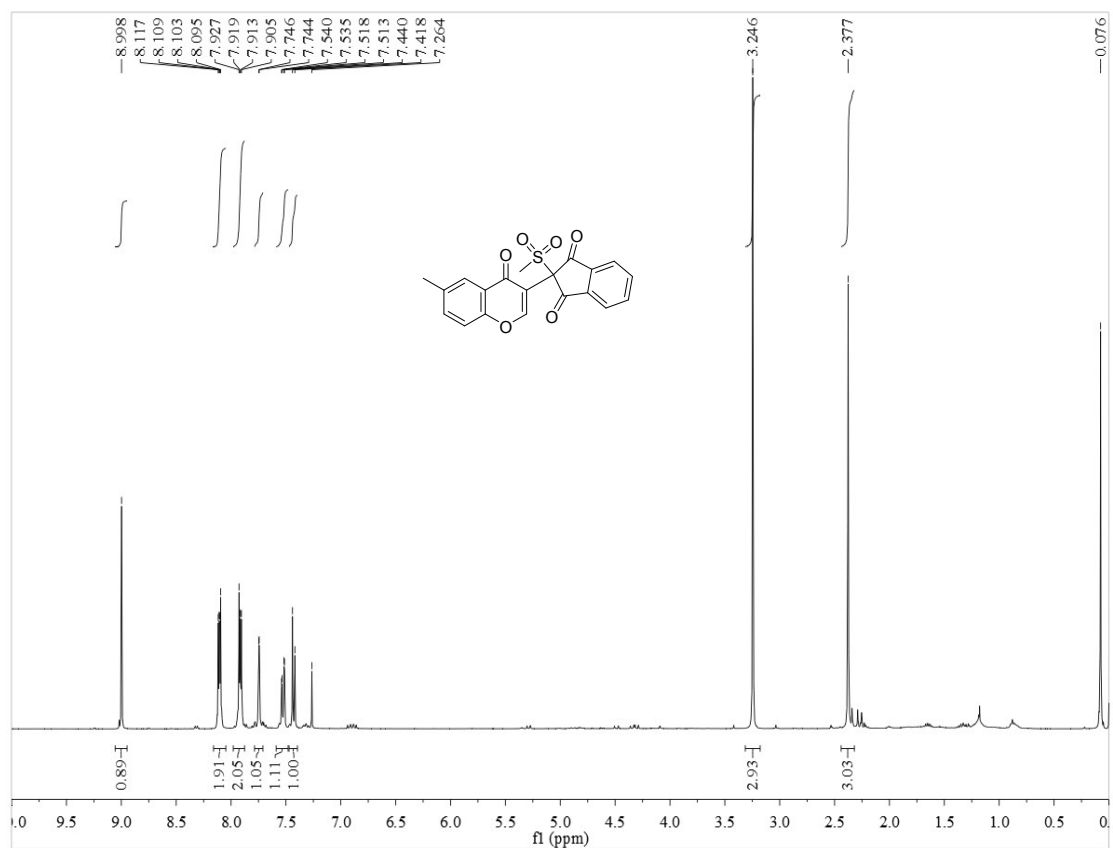
# <sup>1</sup>H and <sup>13</sup>C NMR of 3f



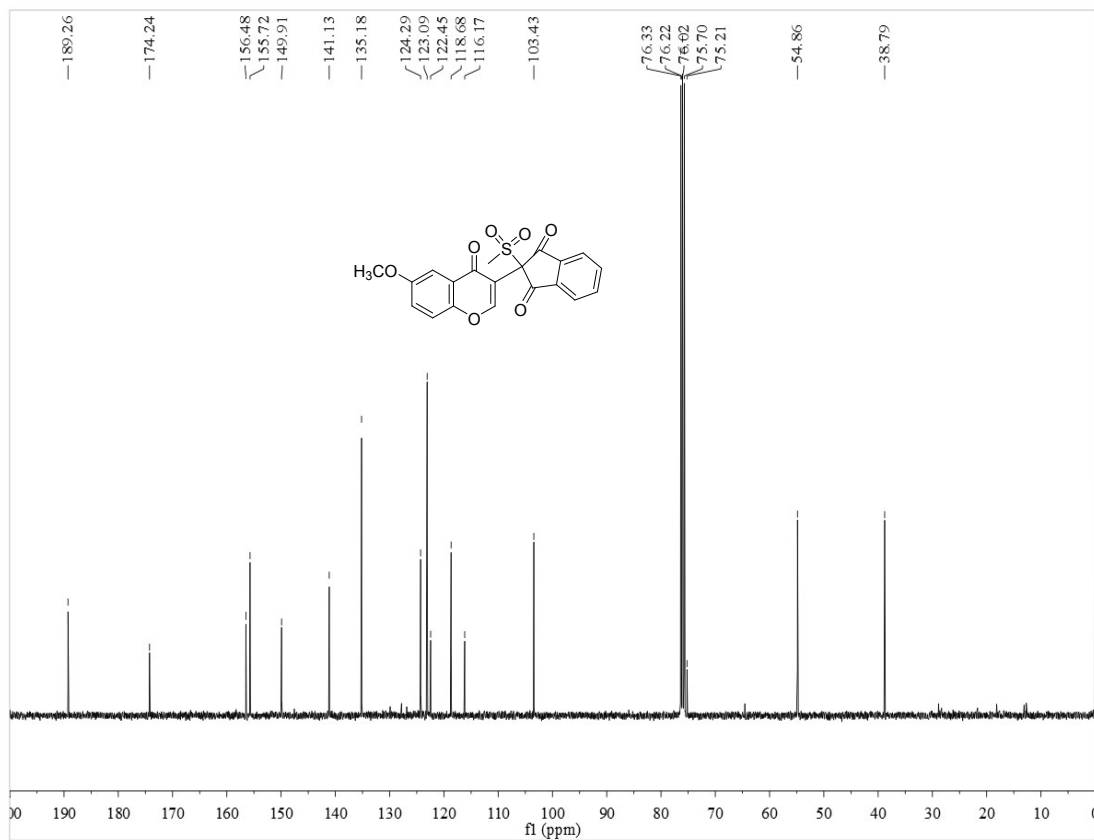
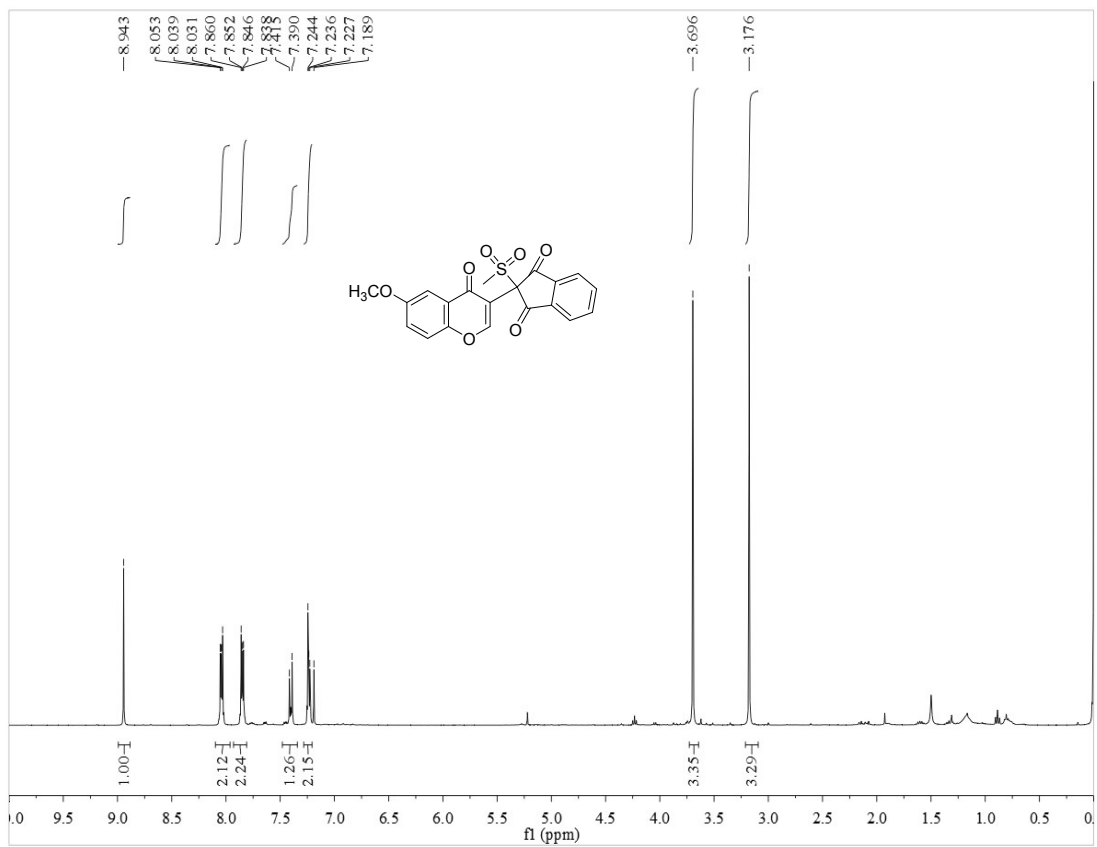
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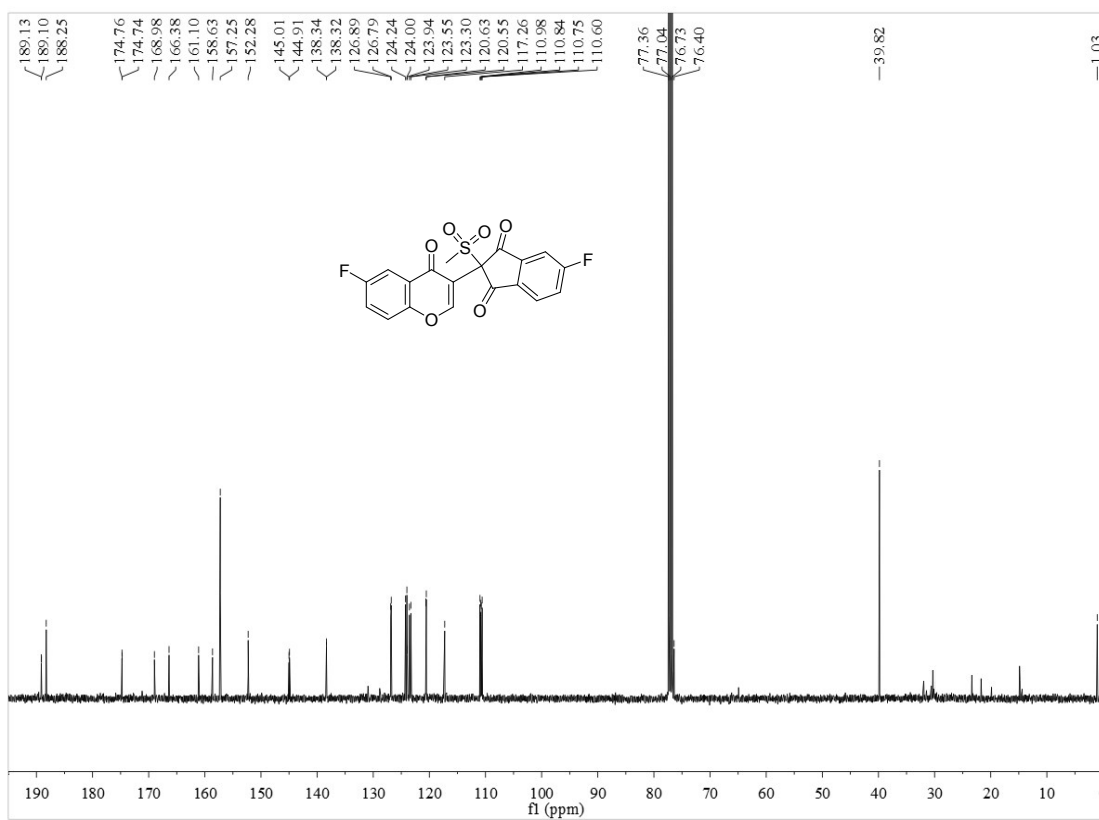
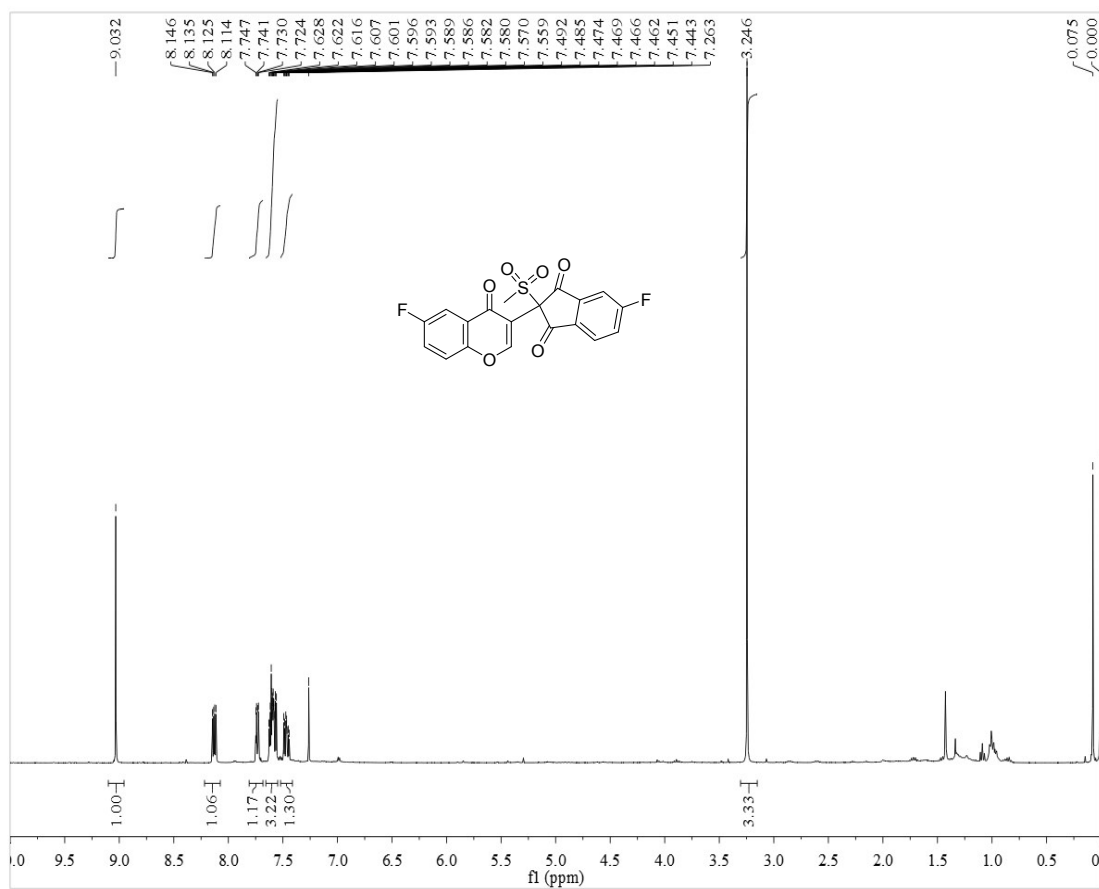
# <sup>1</sup>H and <sup>13</sup>C NMR of 3g



### <sup>1</sup>H and <sup>13</sup>C NMR of 3h



# <sup>1</sup>H and <sup>13</sup>C NMR of 3i

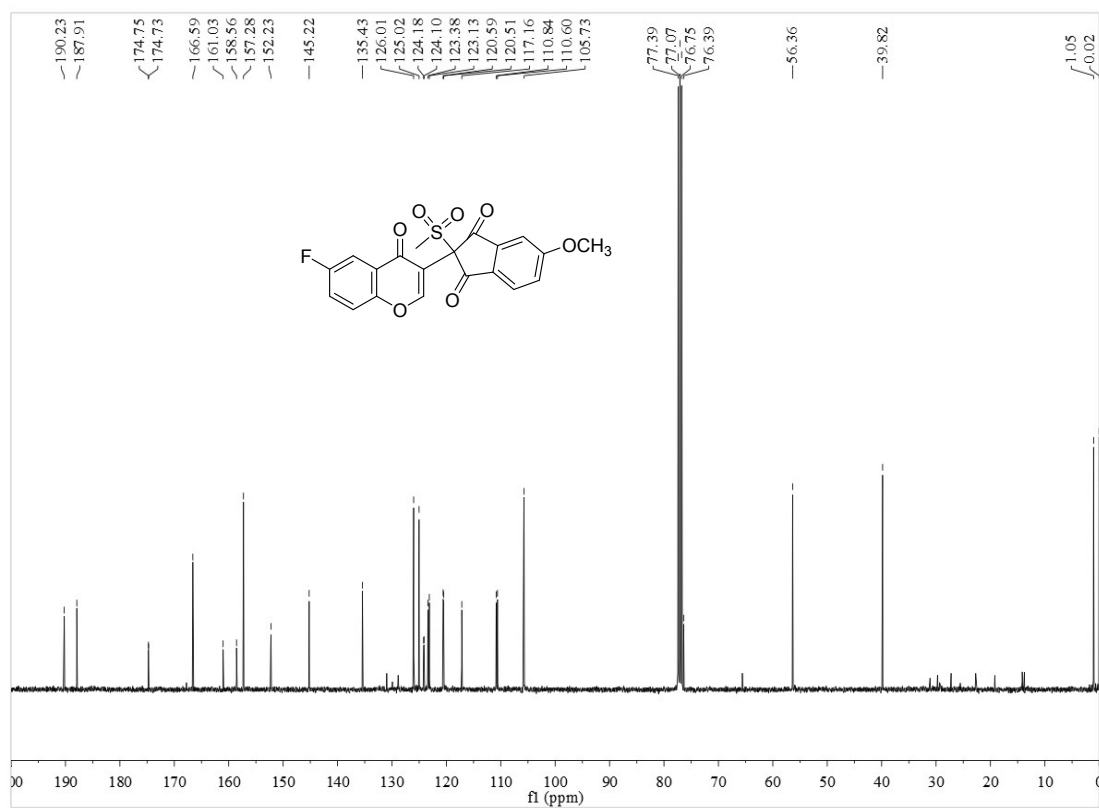
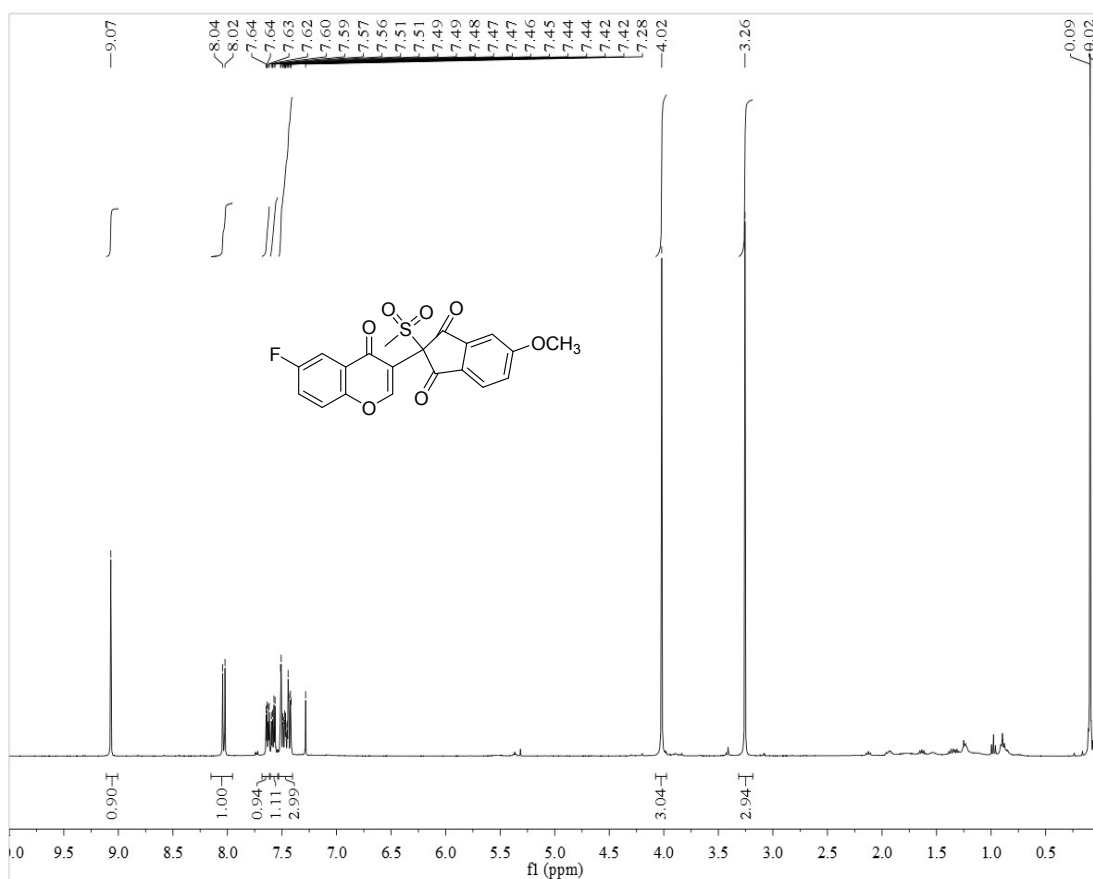


**<sup>19</sup>F NMR of 3i**

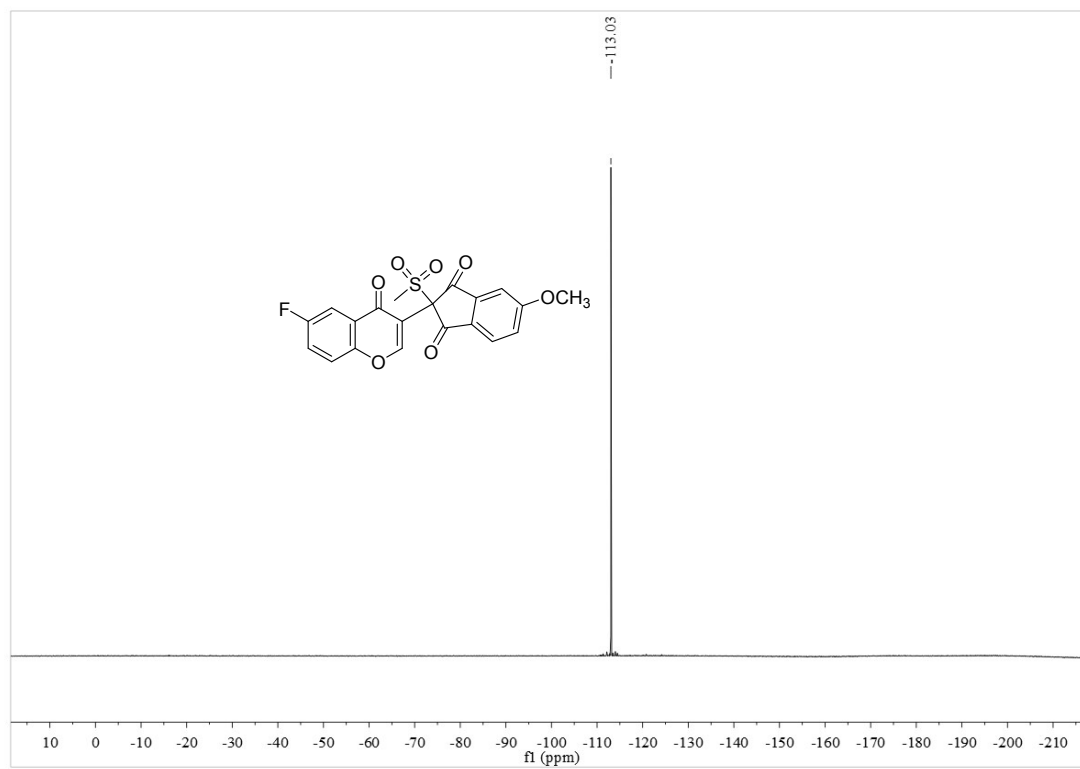




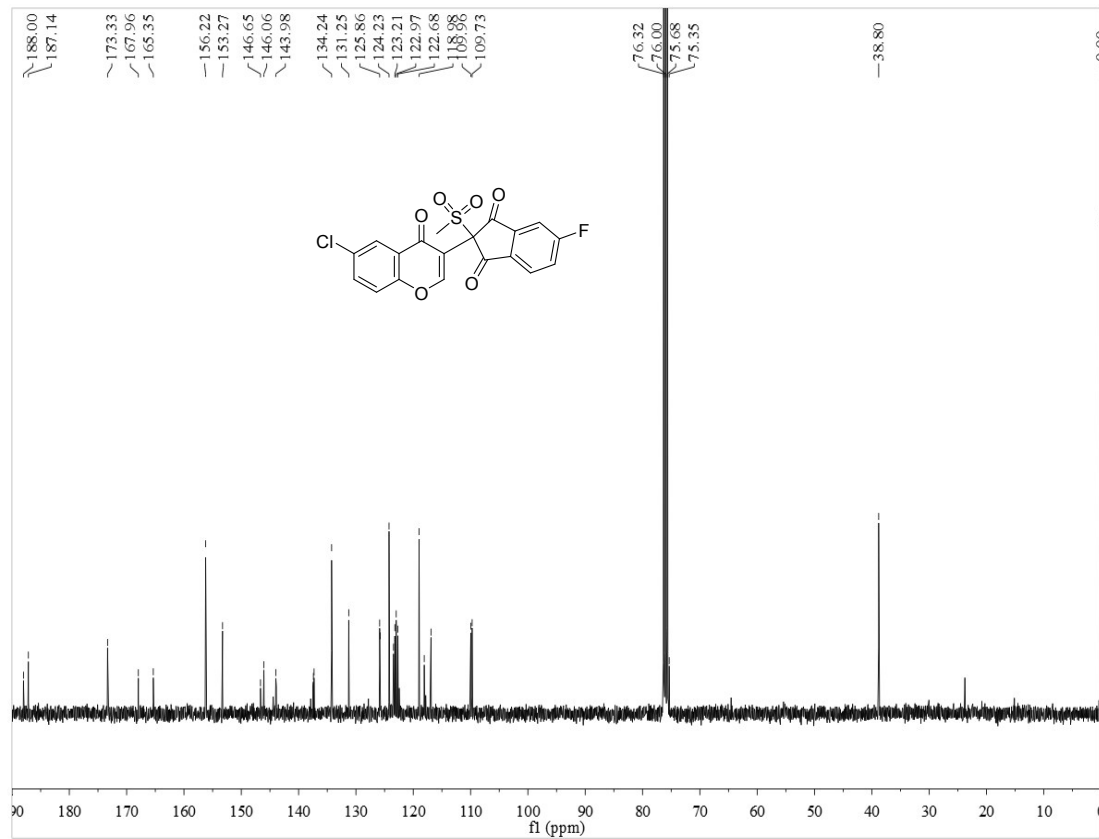
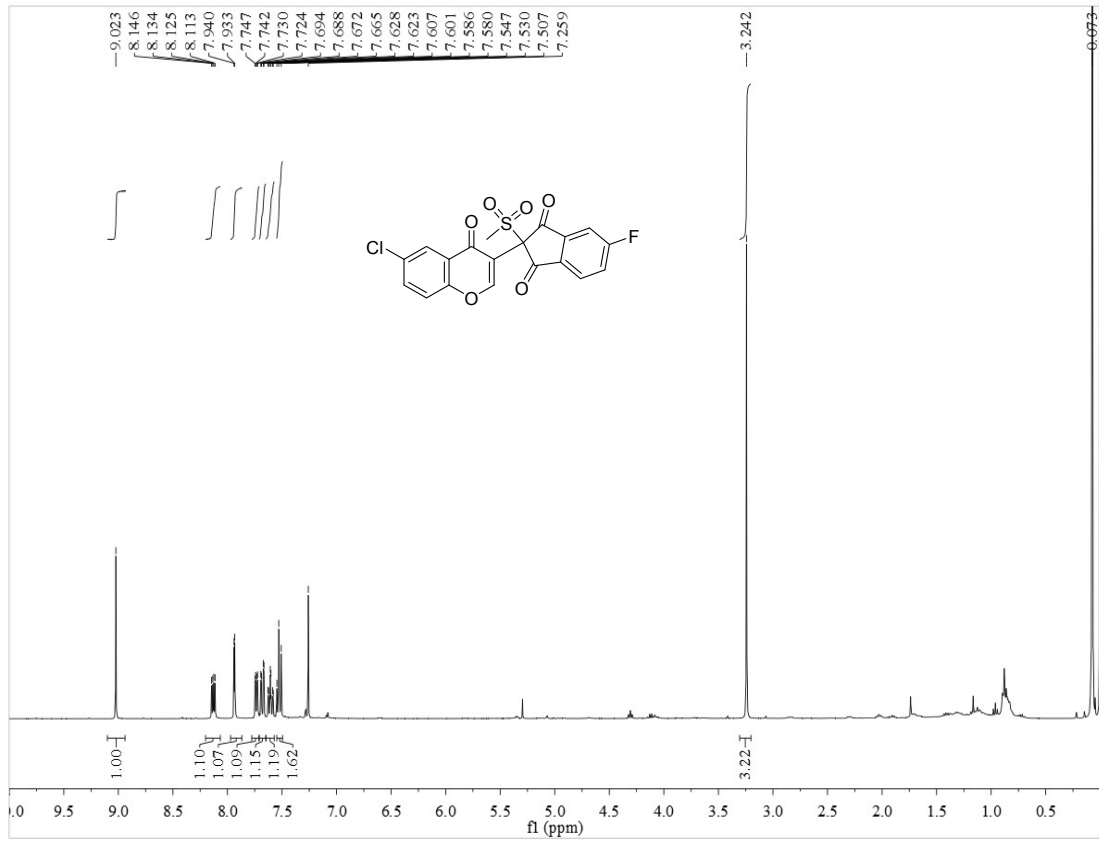
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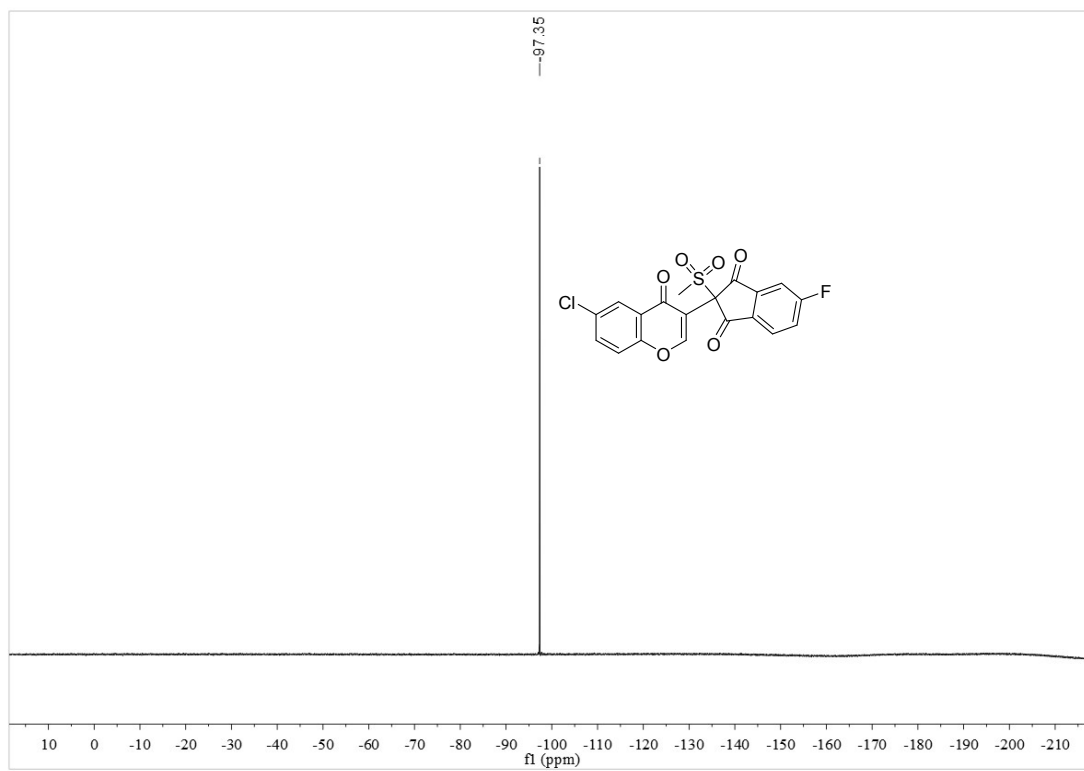
**<sup>19</sup>F NMR of 3j**



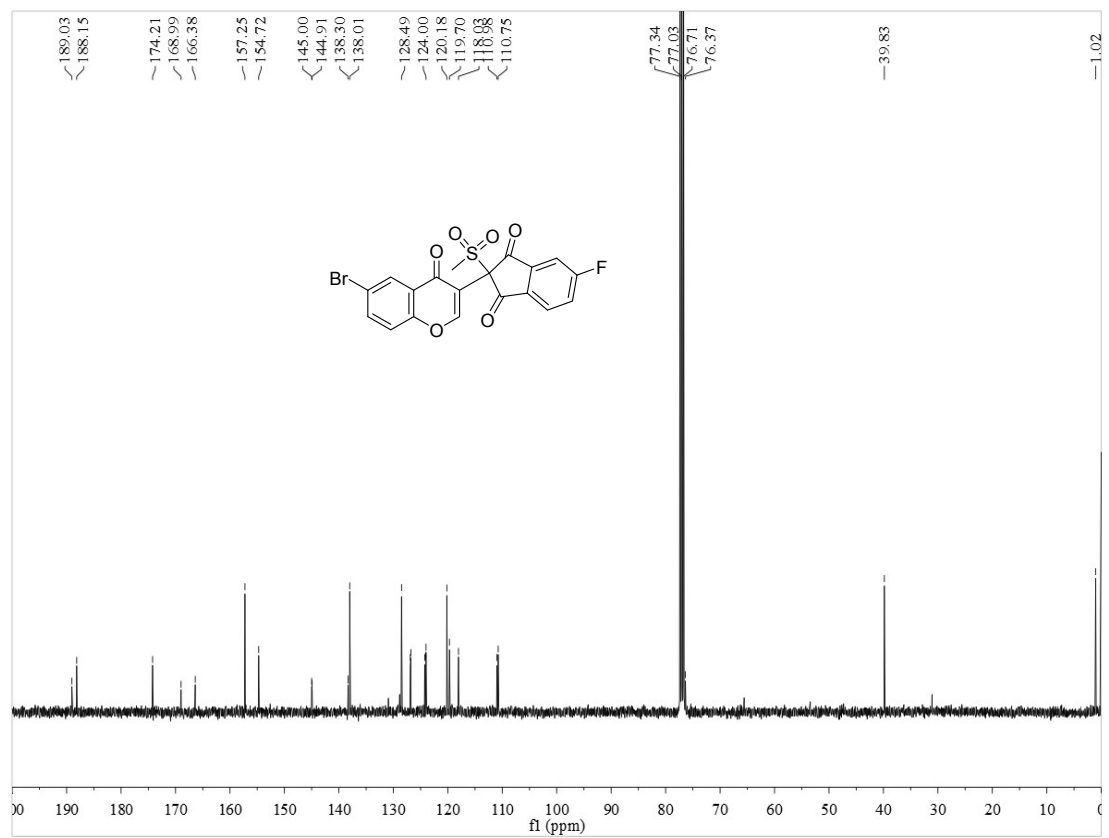
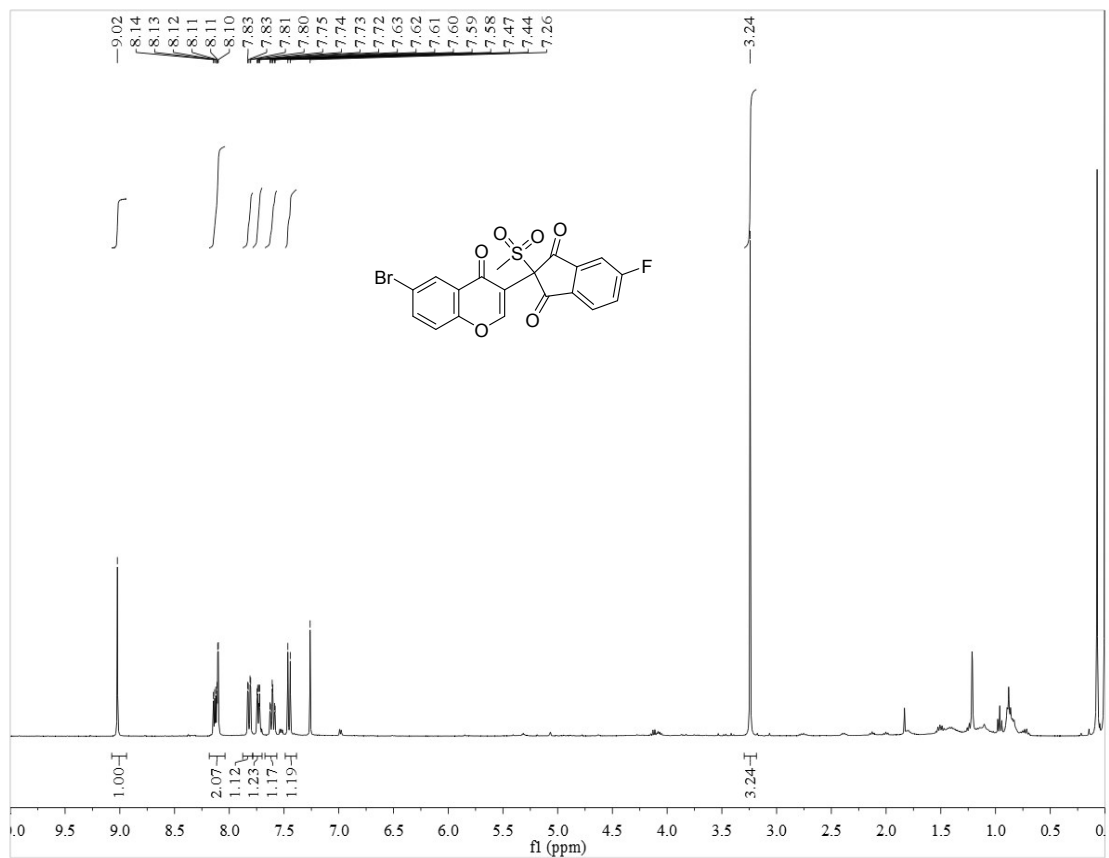
# <sup>1</sup>H and <sup>13</sup>C NMR of 3k



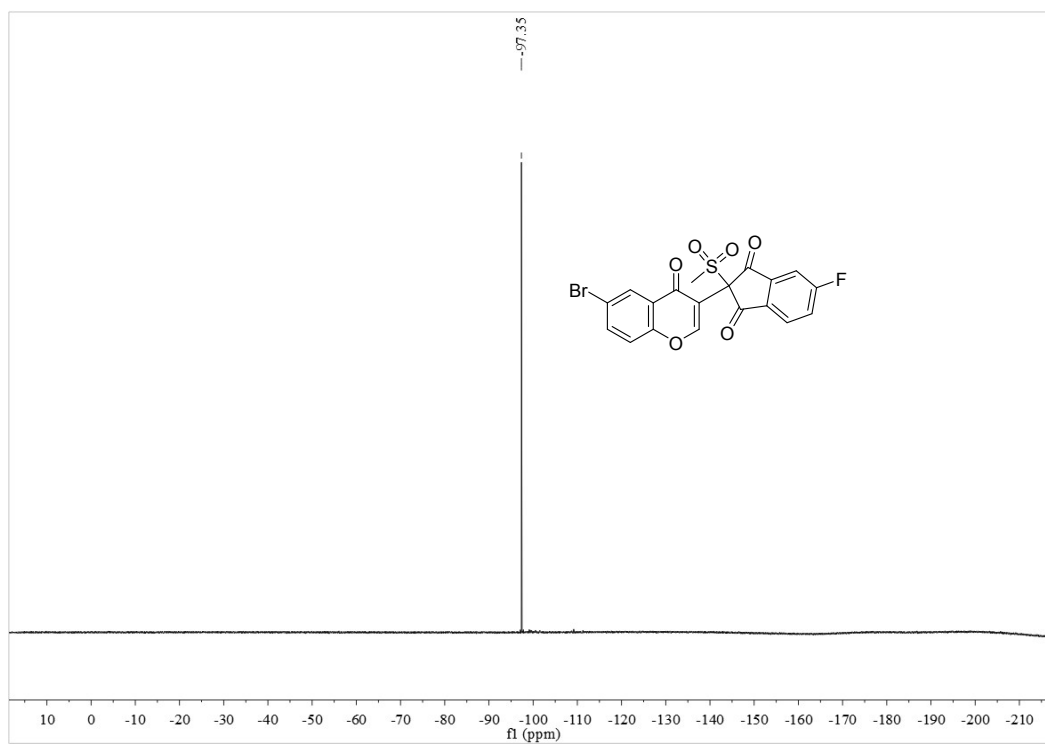
**<sup>19</sup>F NMR of 3k**



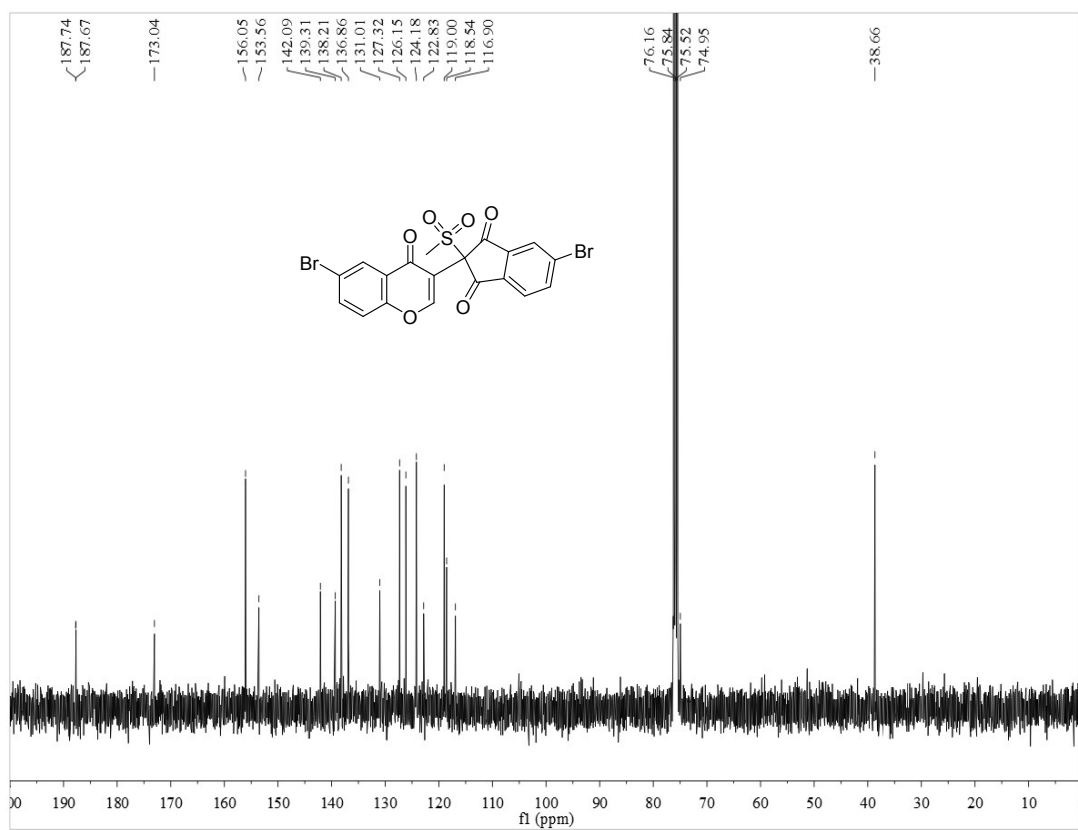
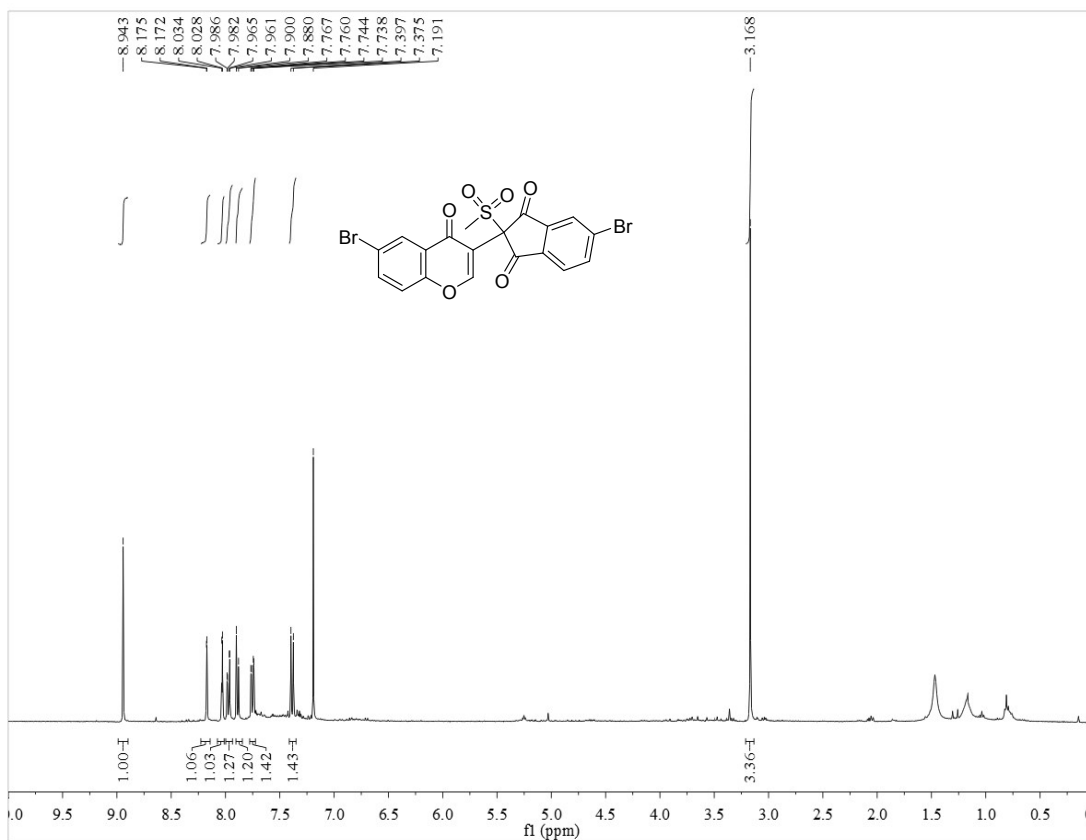
# <sup>1</sup>H and <sup>13</sup>C NMR of 3l



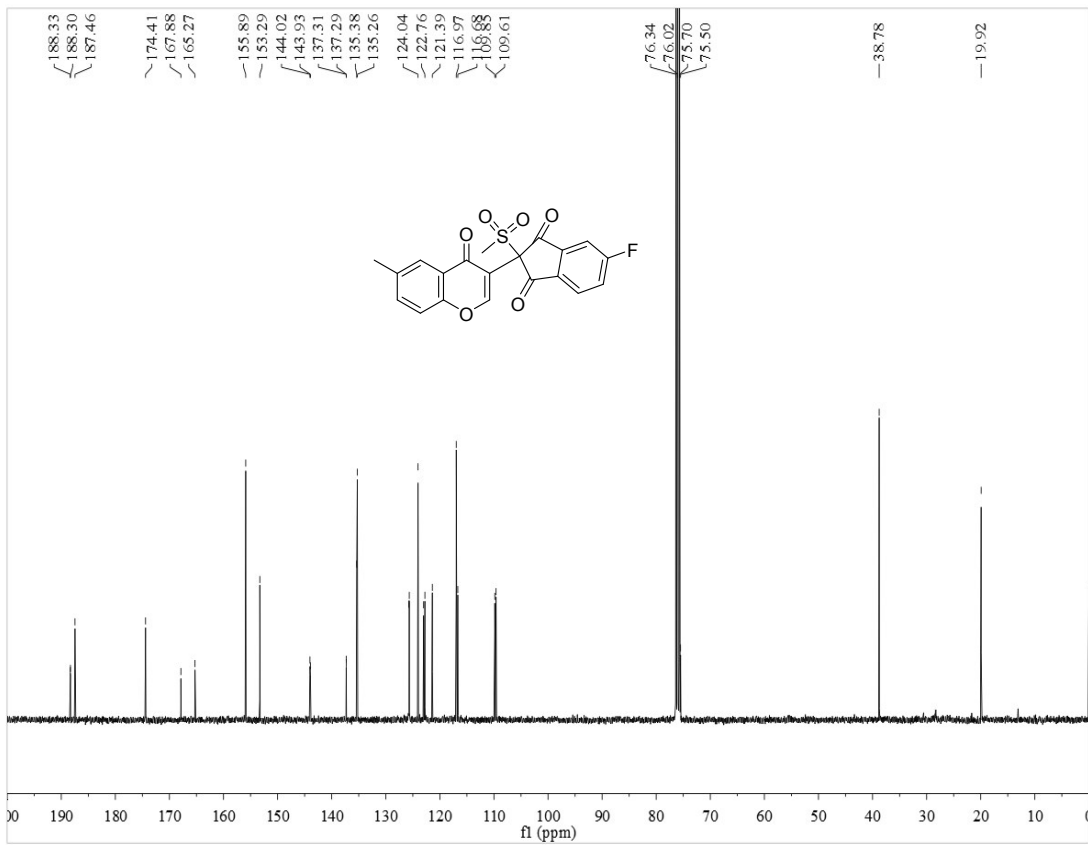
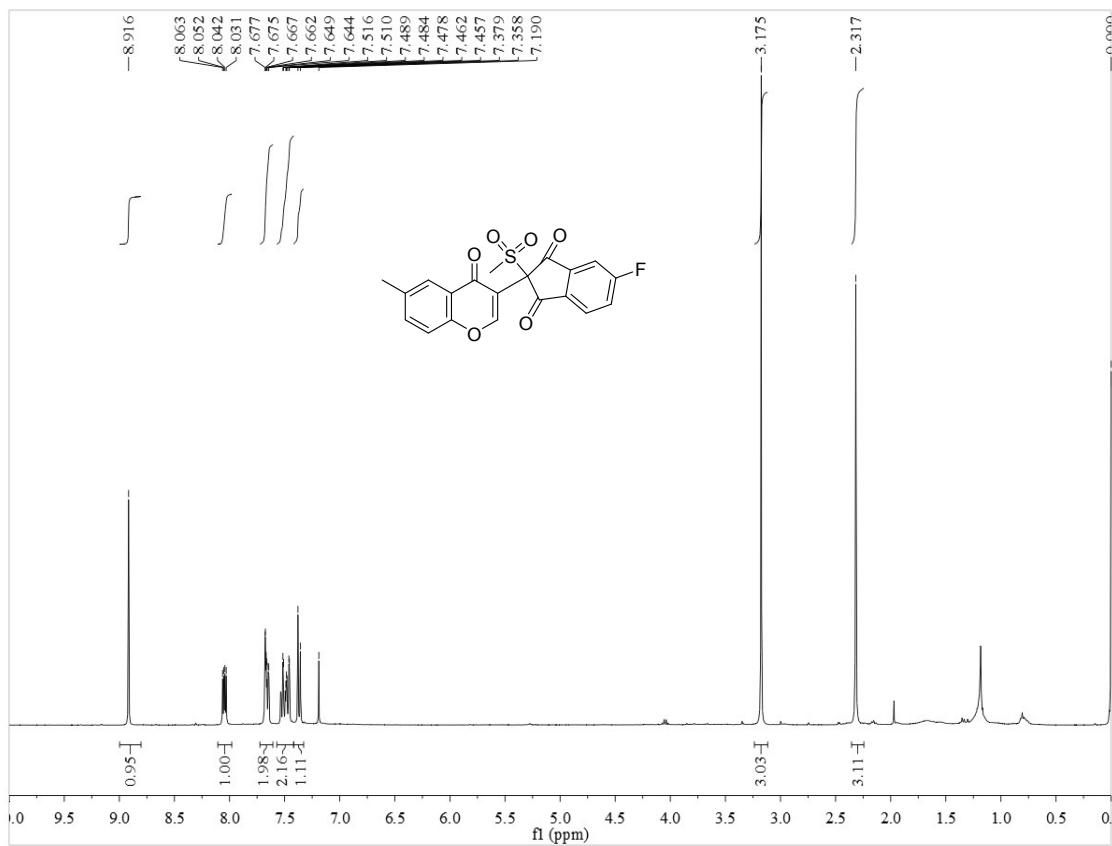
**<sup>19</sup>F NMR of 31**



# <sup>1</sup>H and <sup>13</sup>C NMR of 3m

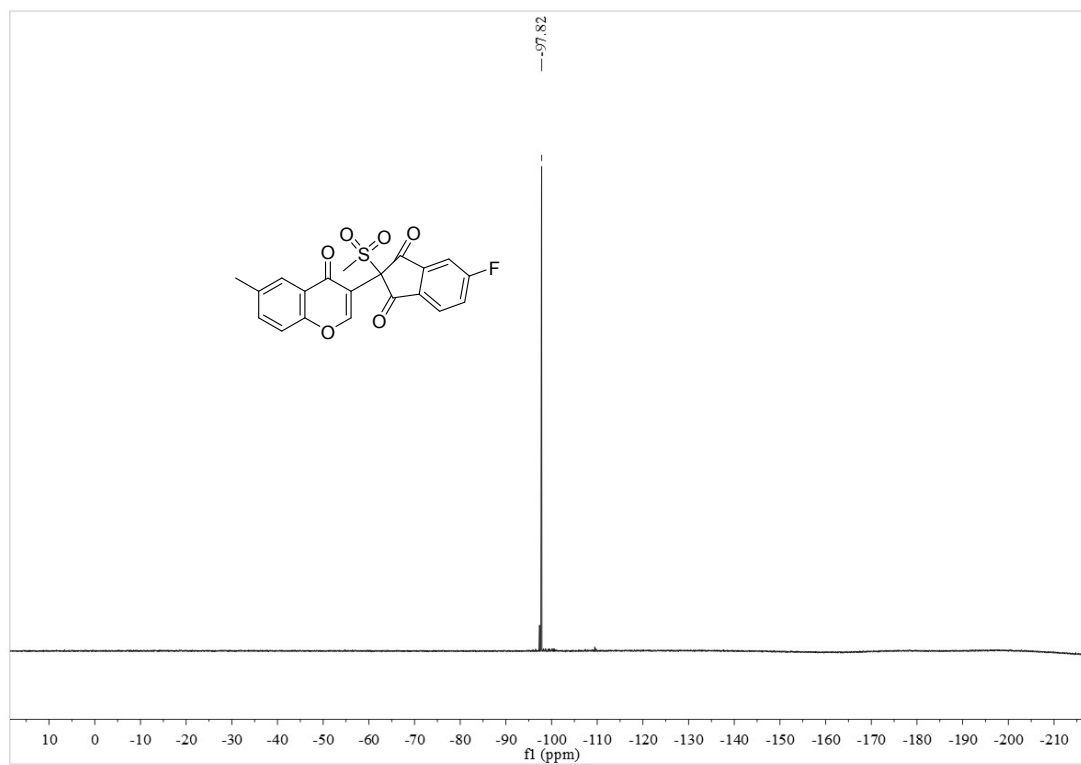


# <sup>1</sup>H and <sup>13</sup>C NMR of 3n

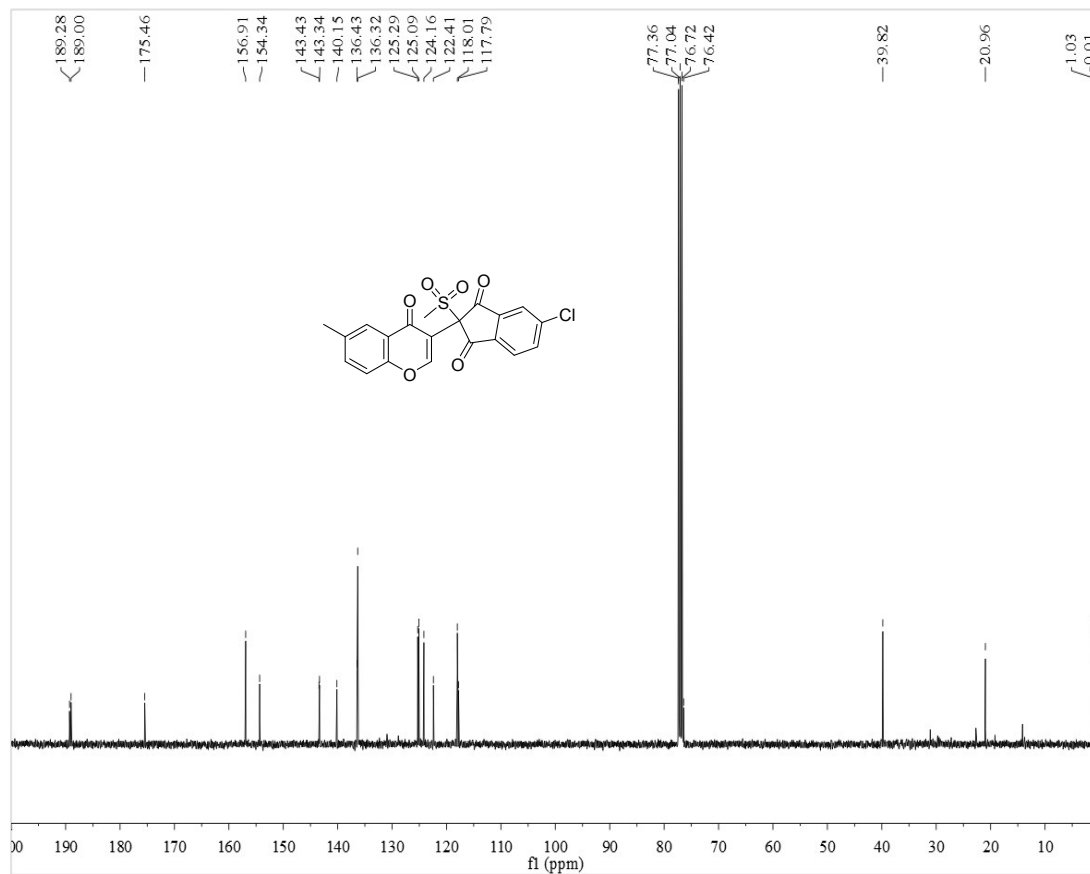
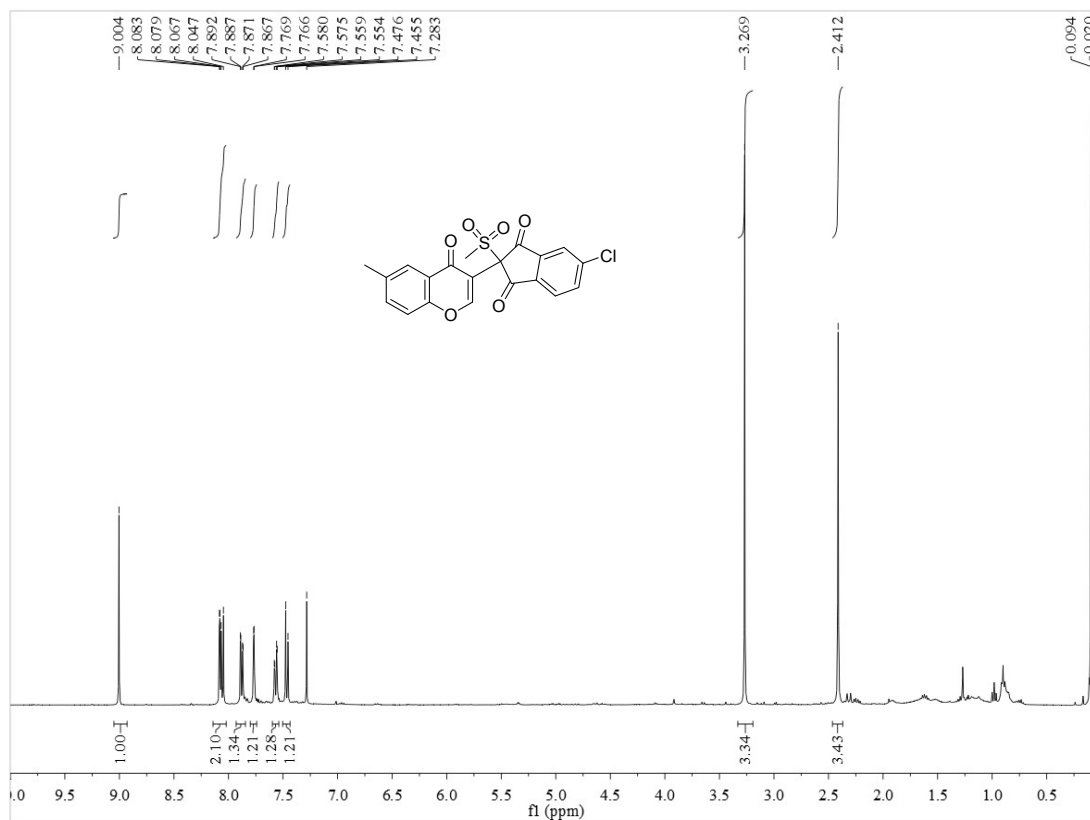




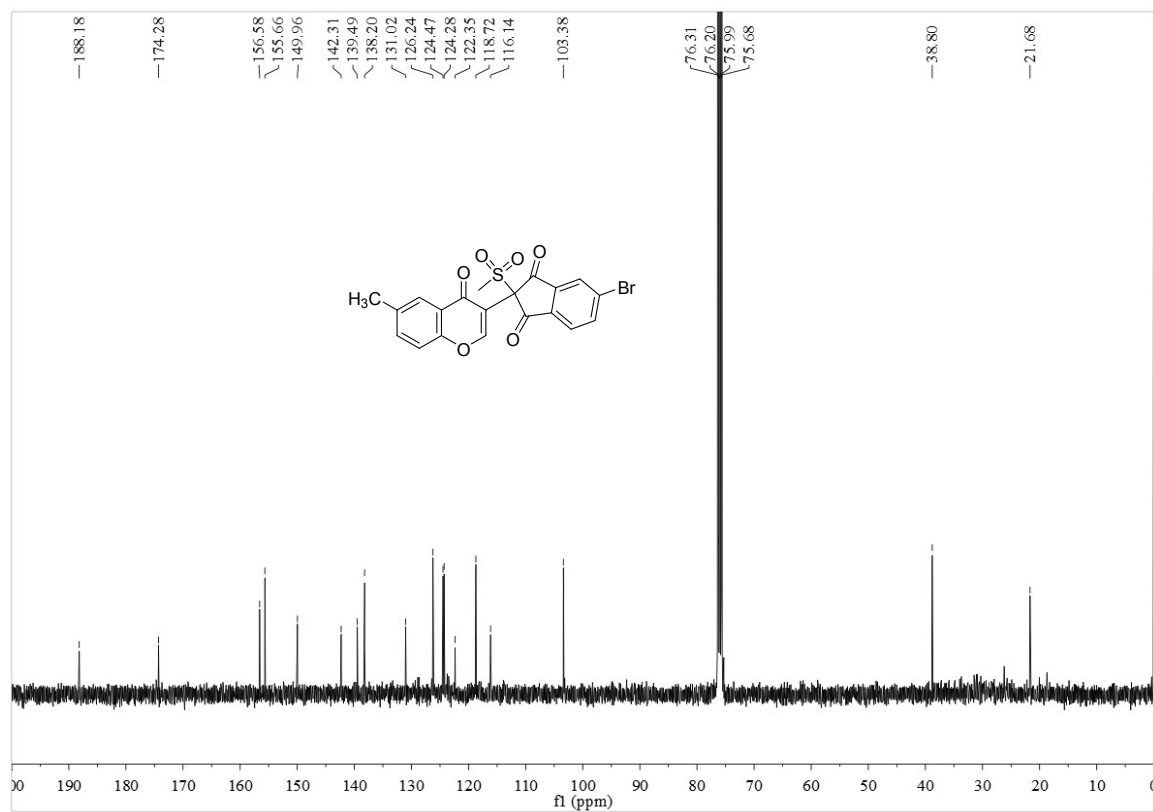
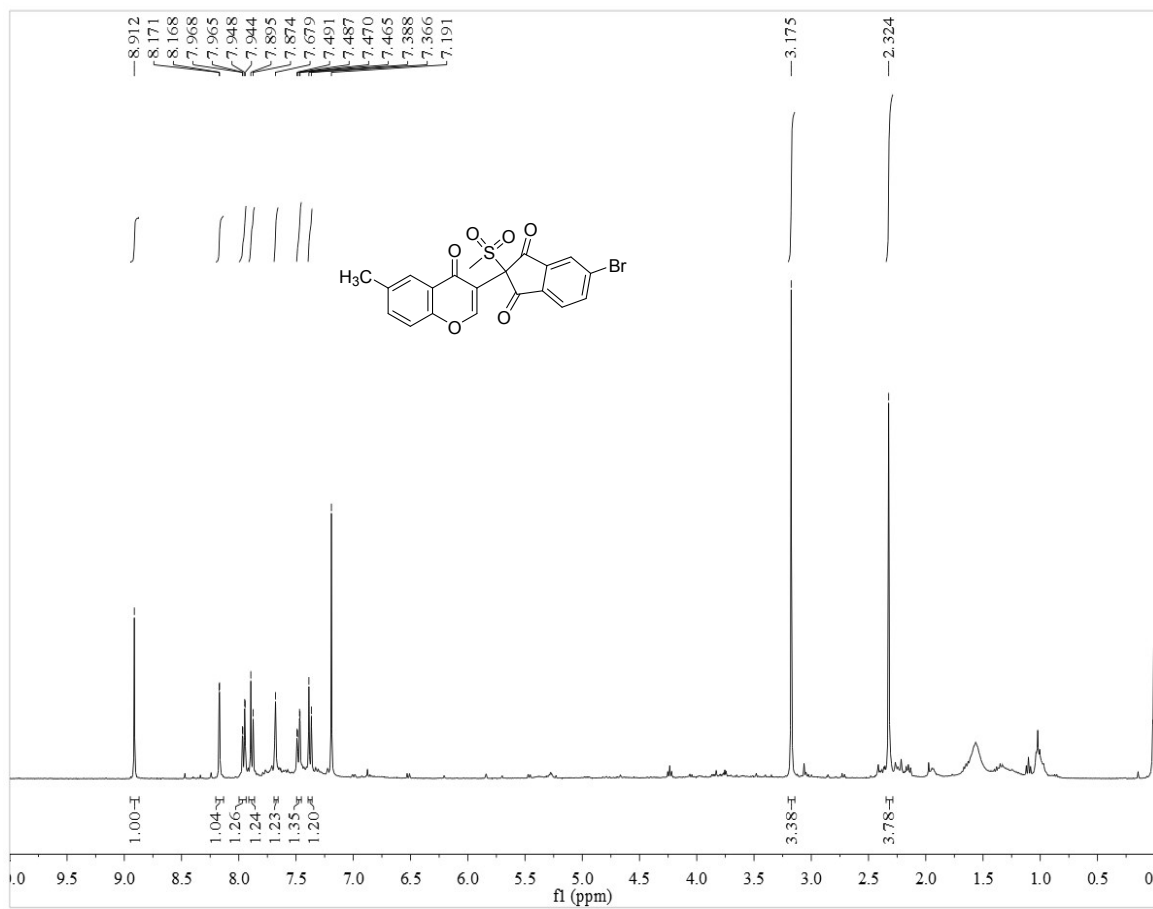
**<sup>19</sup>F NMR of 3n**



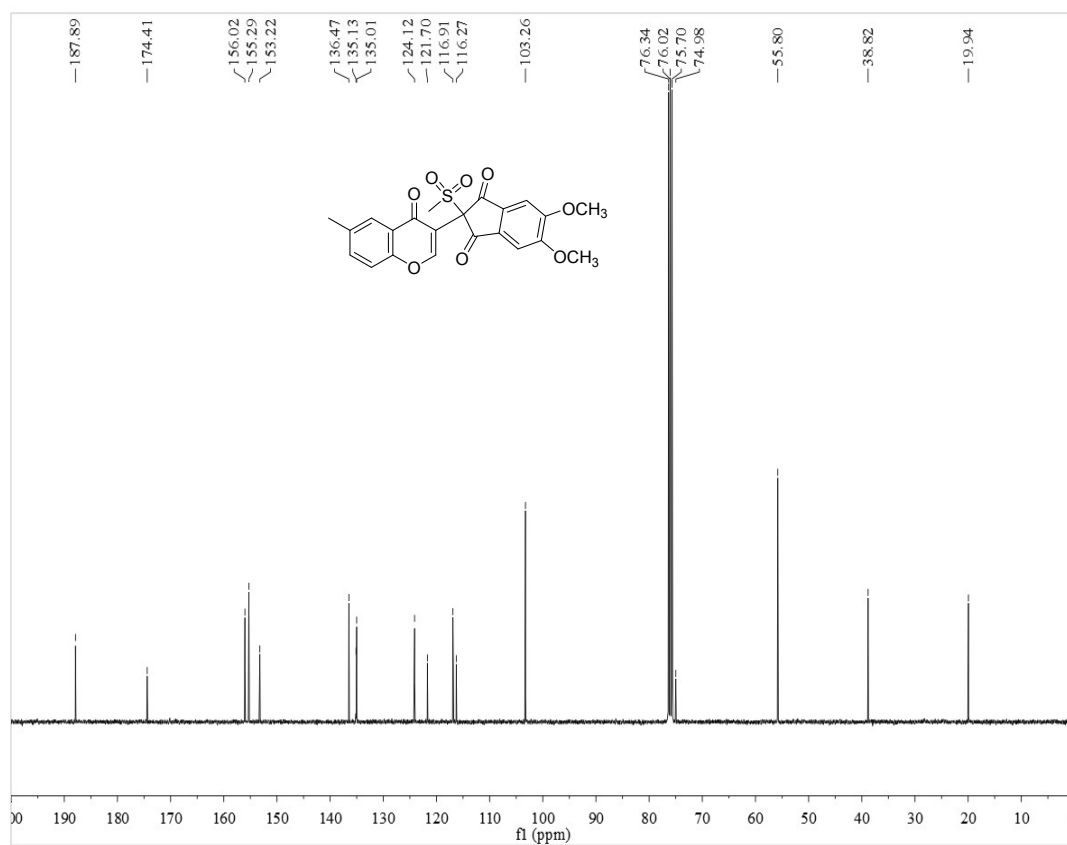
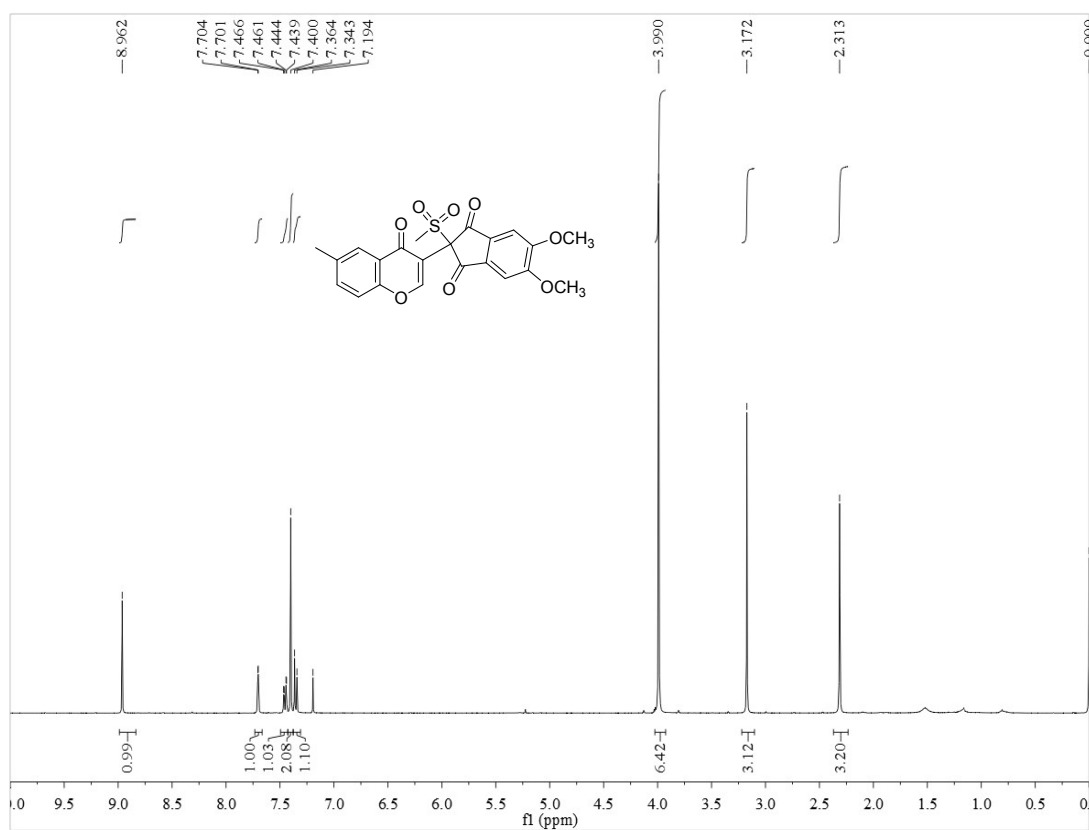
# <sup>1</sup>H and <sup>13</sup>C NMR of 3o



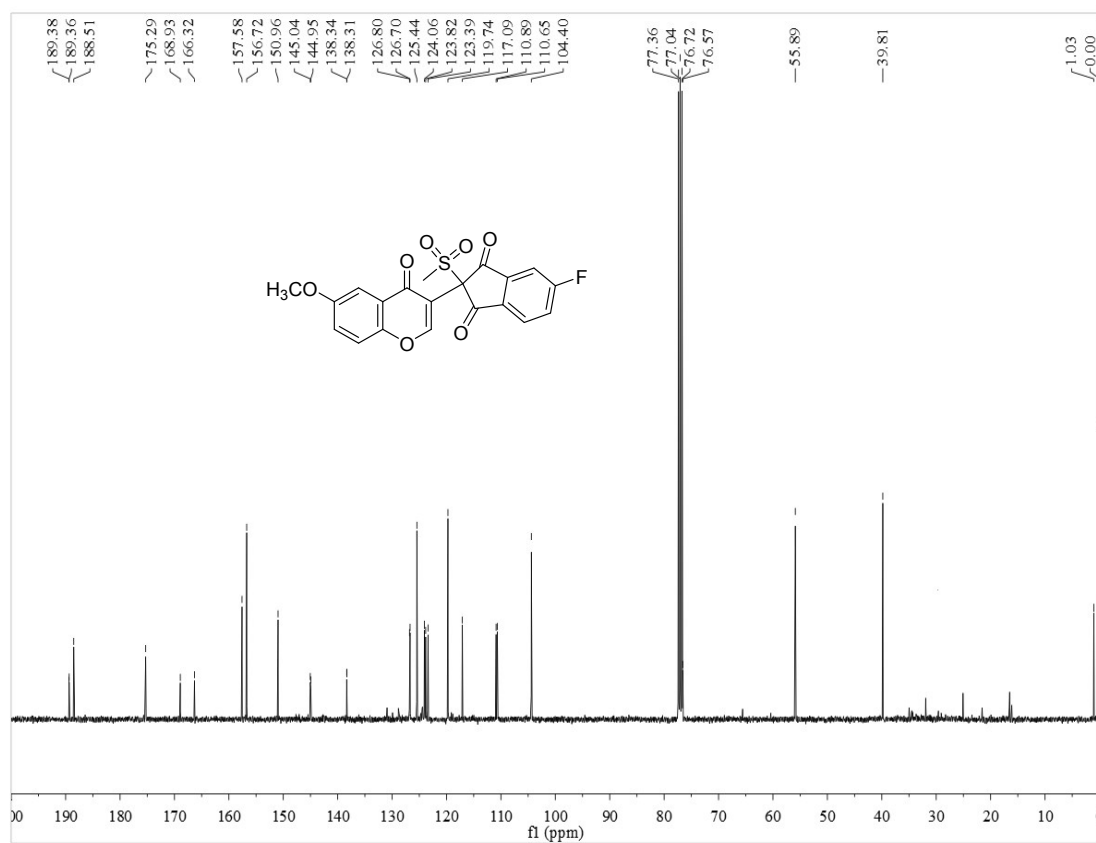
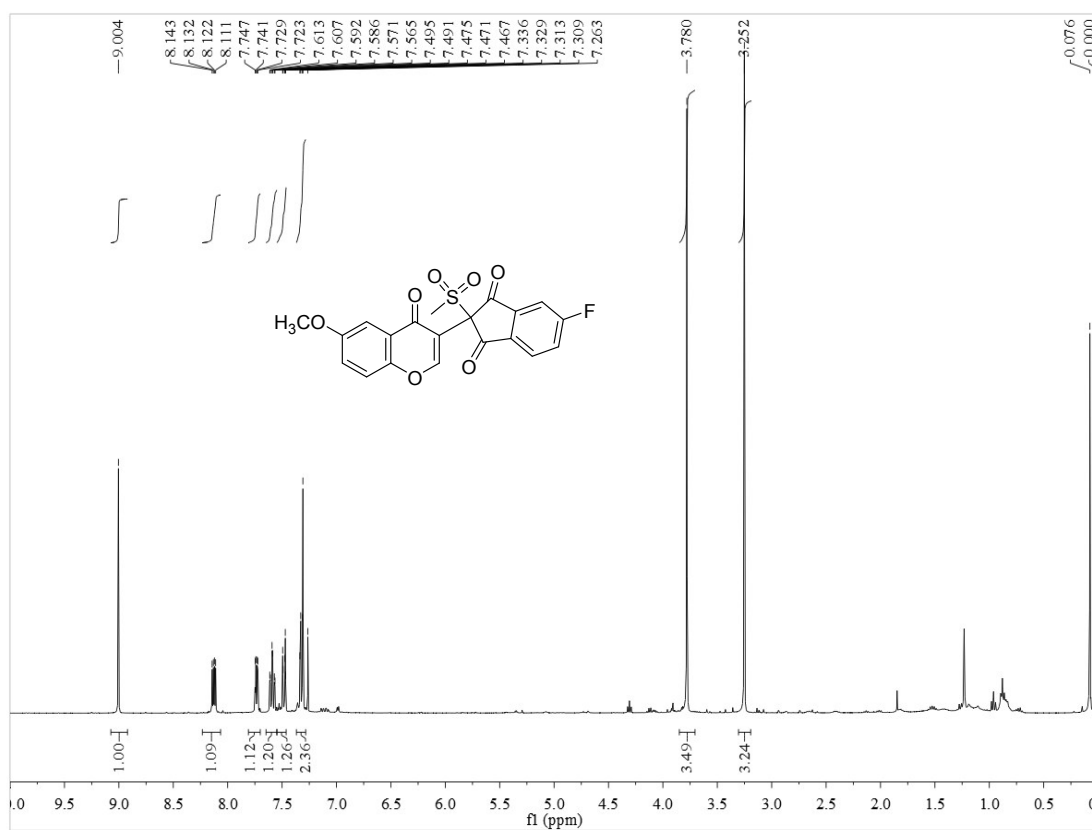
### <sup>1</sup>H and <sup>13</sup>C NMR of 3p



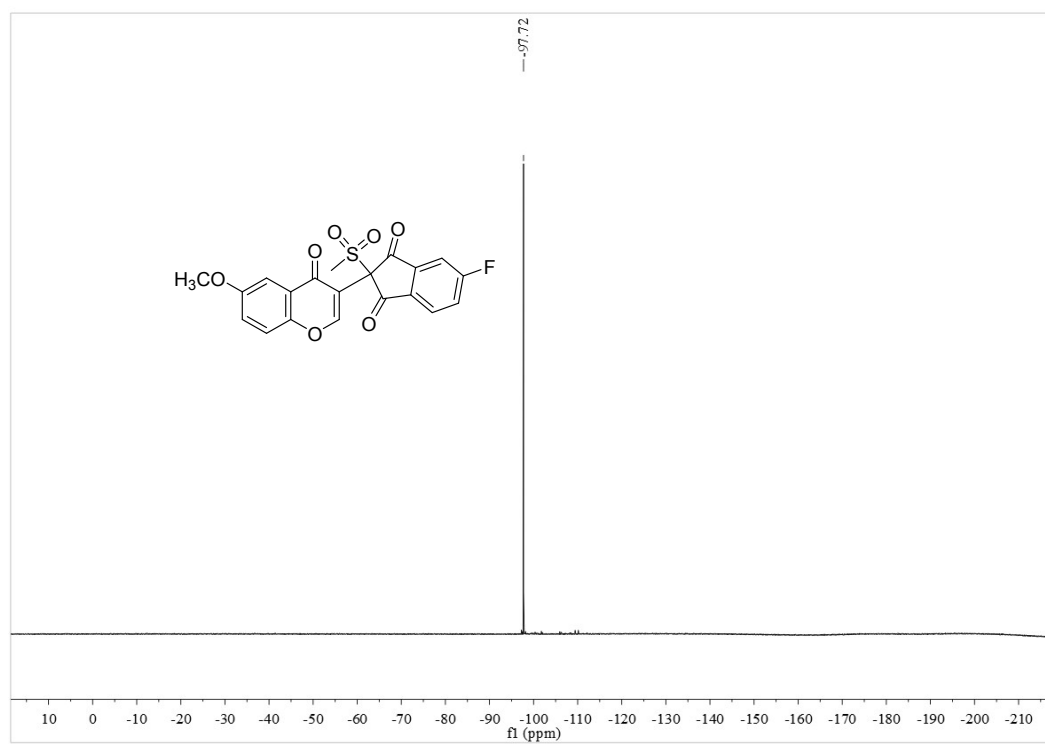
# <sup>1</sup>H and <sup>13</sup>C NMR of 3q



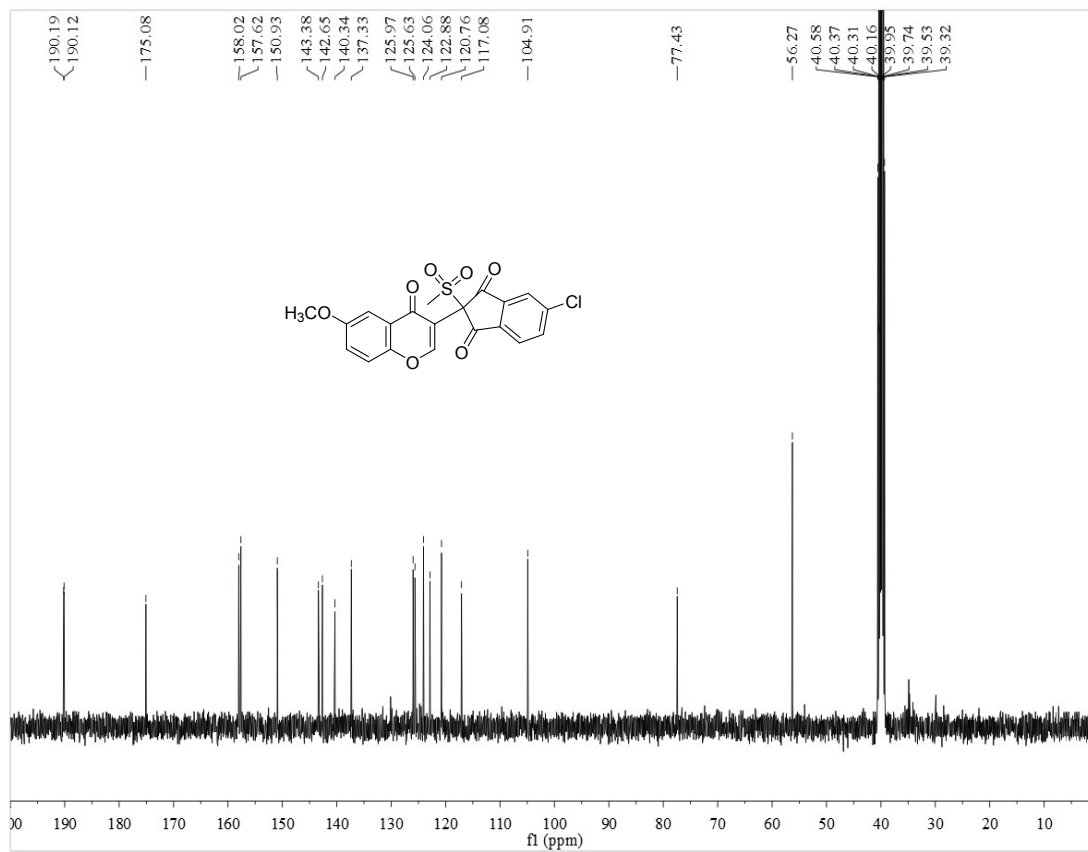
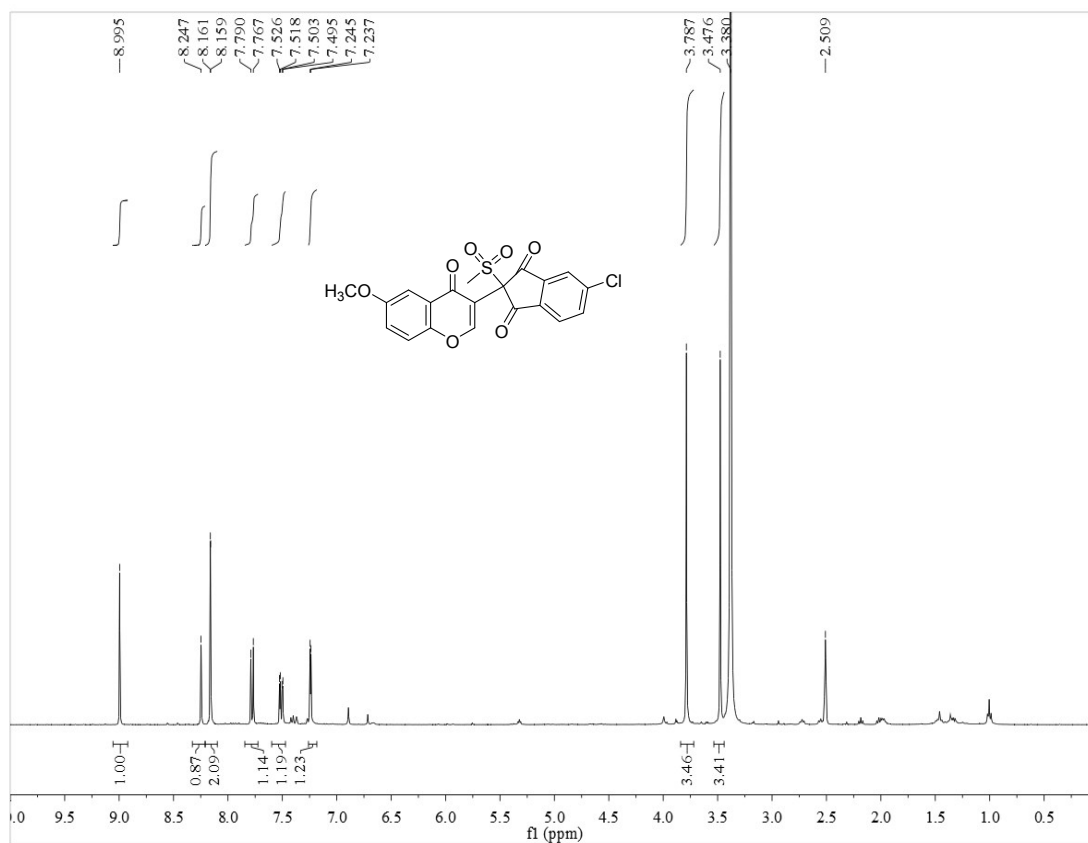
# <sup>1</sup>H and <sup>13</sup>C NMR of 3r



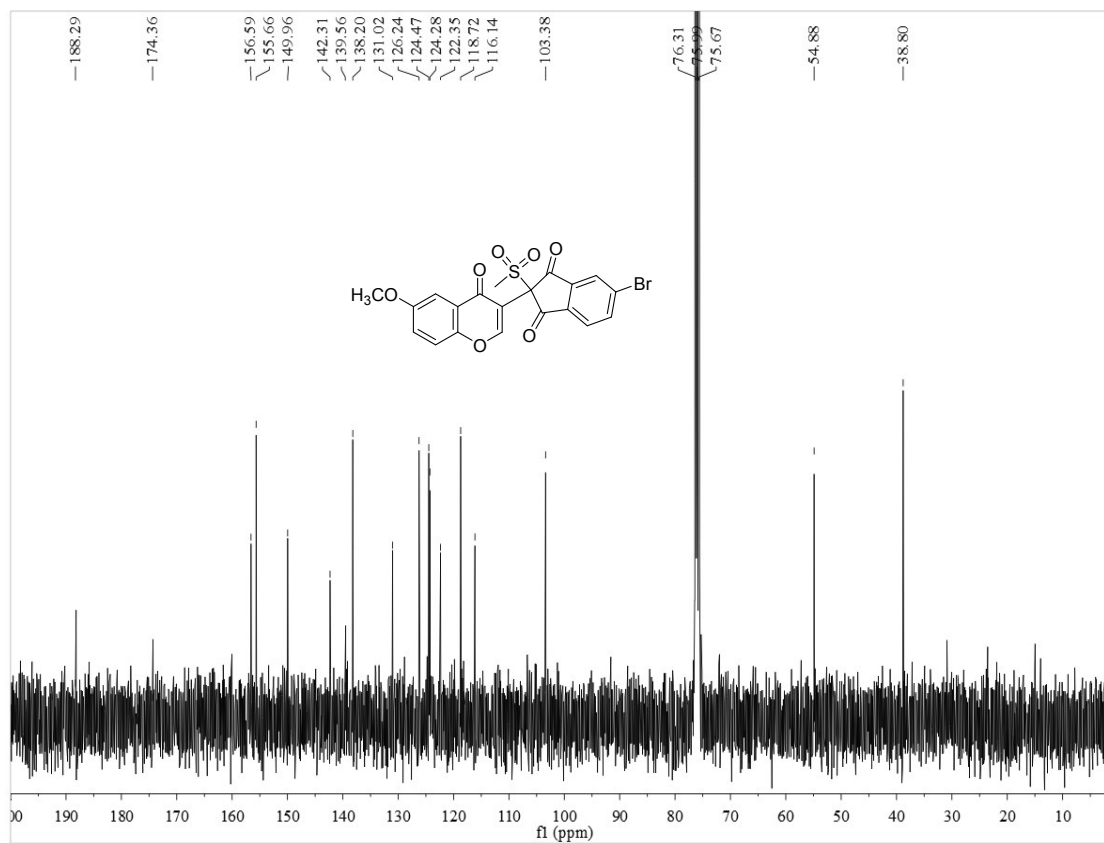
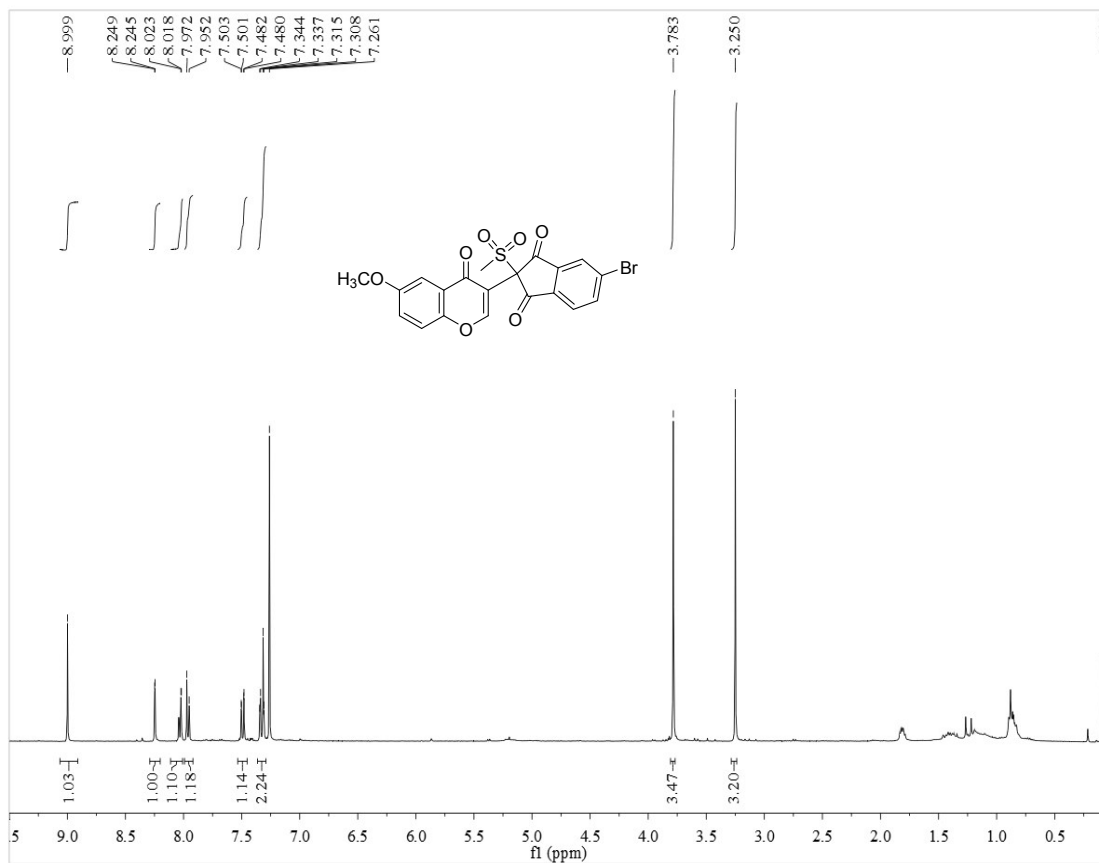
**<sup>19</sup>F NMR of 3r**



# <sup>1</sup>H and <sup>13</sup>C NMR of 3s



# <sup>1</sup>H and <sup>13</sup>C NMR of 3t





# <sup>1</sup>H and <sup>13</sup>C NMR of 3u

