Supporting Information for:

# NaH Promoted One-Pot Tandem Reactions of 3-(1-Alkynyl) Chromones to Form 2-Nitrogen-Substituted Xanthones

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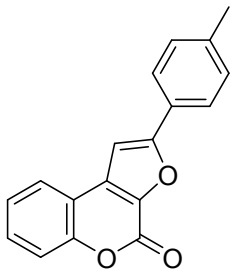
1. Initial attempts in investigation of isocyanoacetates and 3-(1-alkynyl)-chromones

**Table S1: Initial attempts in investigation of isocyanoacetates and 3-(1-alkynyl)-chromones[a]**

| Entry | Condition | Results |
|---|---|---|
| 1 | $Ag_2O$, $Et_3N$, rt | NR, Substrate Recovered |
| 2 | DMF, DBU, AgOTf, $Sc(OTf)_3$, 50℃ | Messy |
| 3 | DMF, CuCl, $Cs_2CO_3$, Ar, 100℃ | Messy |
| 4 | $CH_3CN$, CuCl, Ar, 50℃ | Furocoumarin **A**[b] |
| 5 | MeCN, CuCl, $Cs_2CO_3$, Ar, 50℃ | **3a** |
| 6 | MeCN, CuCl, $Cs_2CO_3$, Ar, rt | **3a** |
| 7 | MeCN, CuCl, $Cs_2CO_3$, Ar, reflux | **3a** |
| 8 | NMP, $Ag_2O$, $K_2CO_3$, MW, 130℃ | Messy |
| 9 | NMP, AgOAc, $K_2CO_3$, MW, 130℃ | **2a** + **3a** |

[a]The reaction were carried out with combinations of 0.1 eq base and 0.01 eq transition metal salt.
[b]The furocoumarin compound was found in the experiment following the route in this literature:
(1) G. Cheng, Y. Hu. *Chem. Commun.* **2007**, *31*, 3285-3287




**A**

**Figure S1:** Stucture of Furocoumarin **A**

2.NMR Spectra

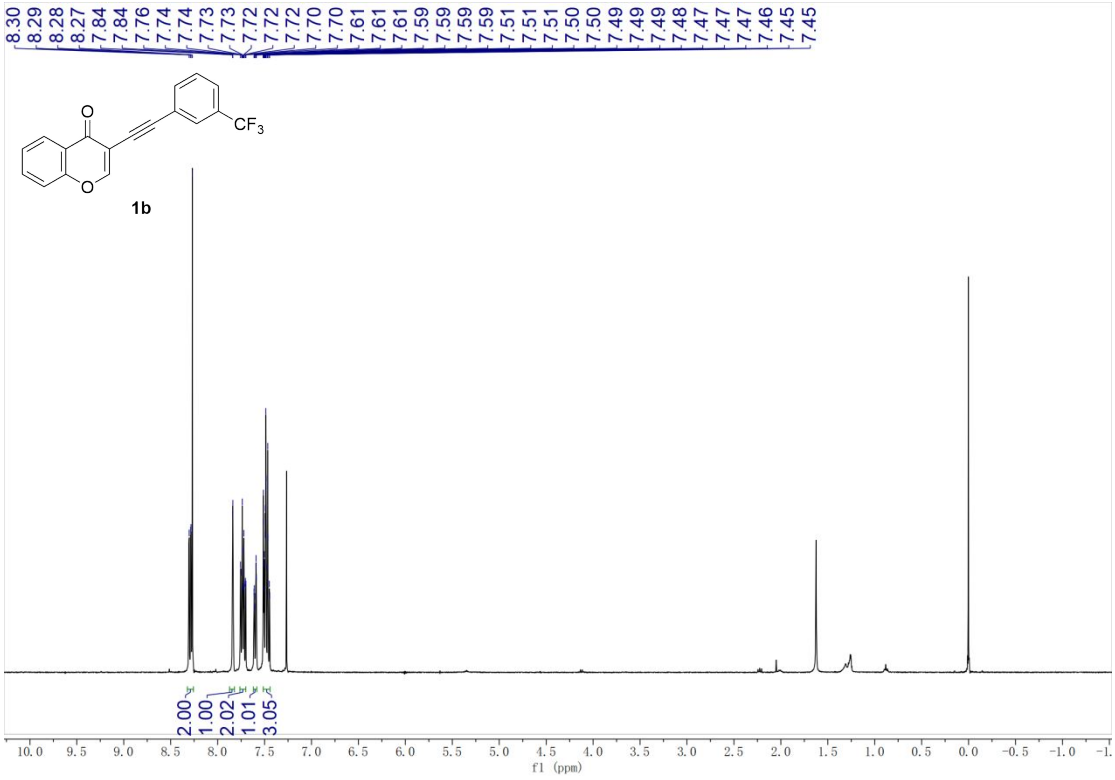



**Figure S2:** $^{1}$H NMR Spectrum of Compound **1b**(400 MHz, $CDCl_3$)

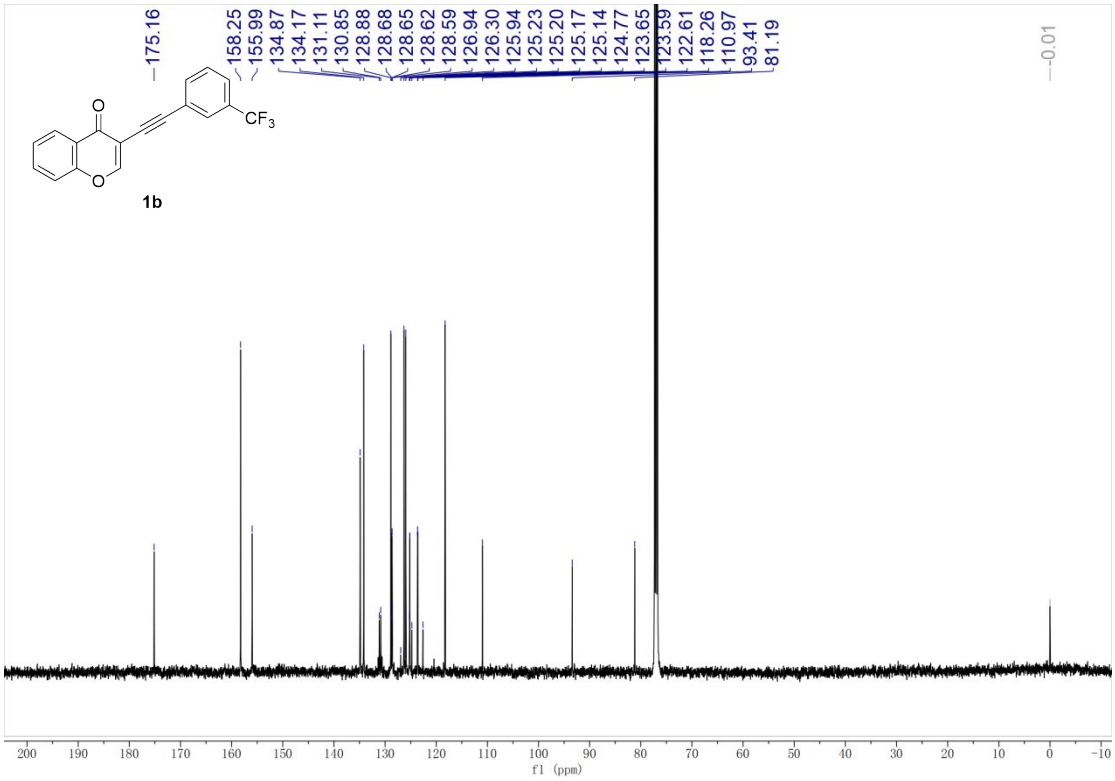



**Figure S3:** $^{13}$C NMR Spectrum of Compound **1b**(125 MHz, $CDCl_3$)

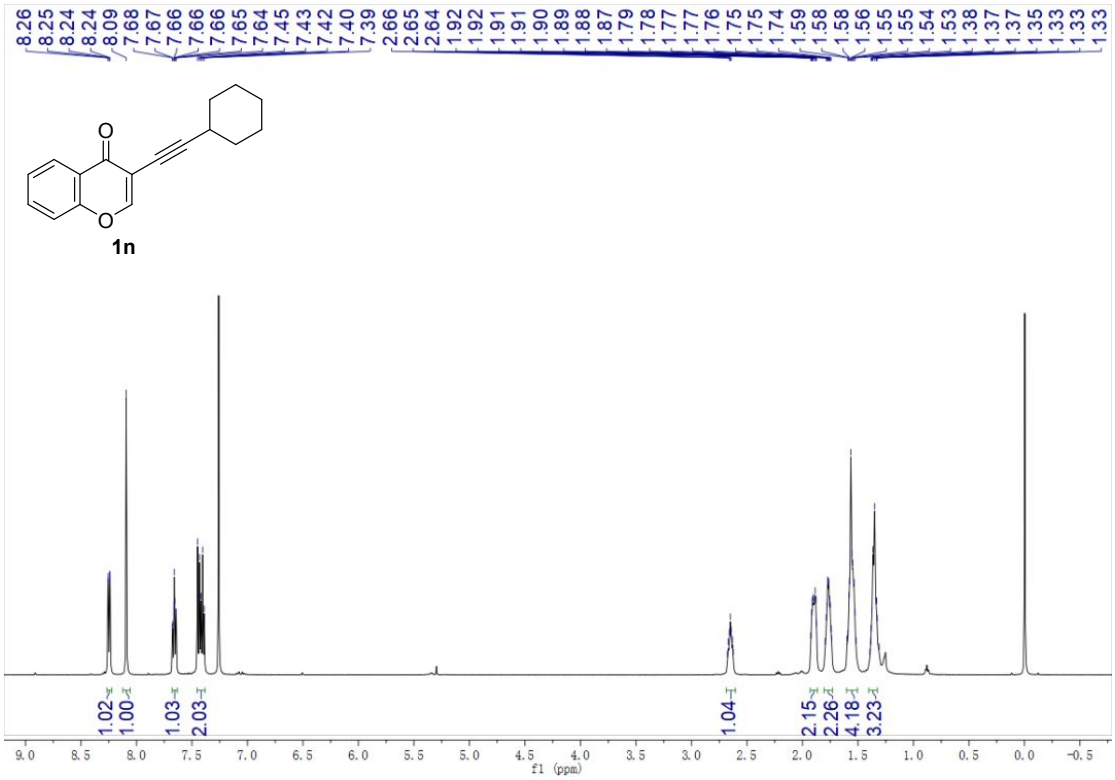



**Figure S4:** $^{1}$H NMR Spectrum of Compound **1n**(500 MHz, $CDCl_3$)

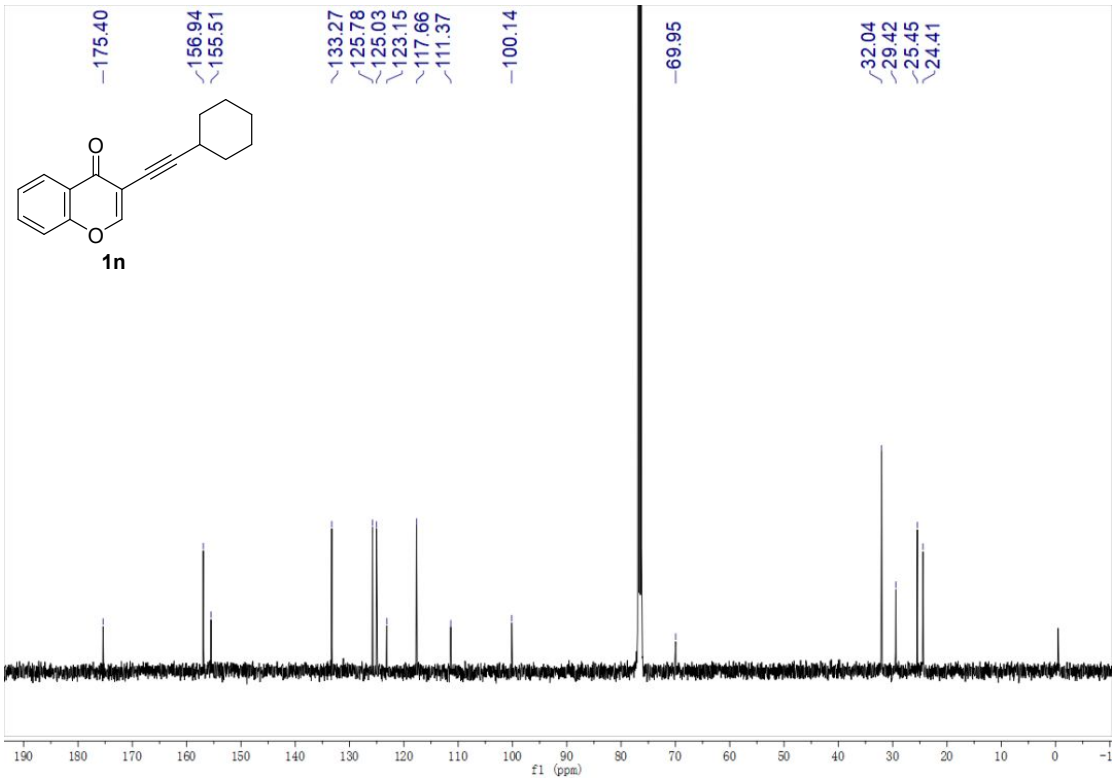



**Figure S5:** $^{13}$C NMR Spectrum of Compound **1n**(125 MHz, $CDCl_3$)

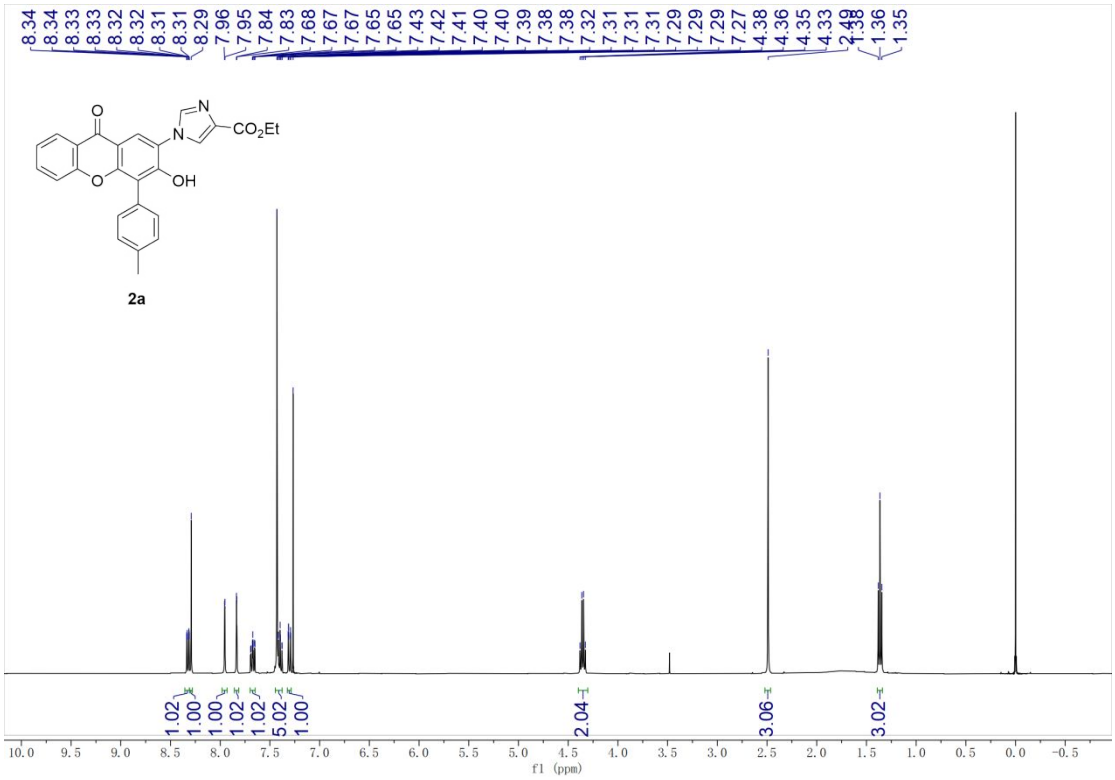



**Figure S6:** $^{1}$H NMR Spectrum of Compound **2a**(400 MHz, $CDCl_3$)

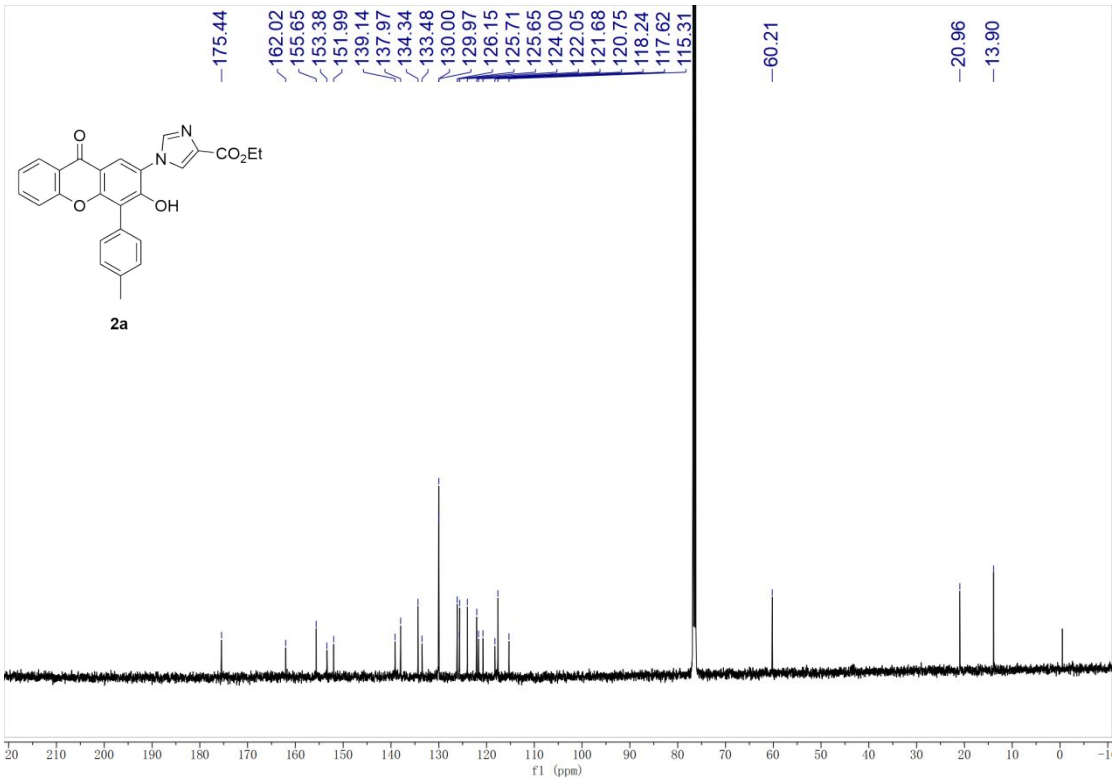



**Figure S7:** $^{13}$C NMR Spectrum of Compound **2a**(125 MHz, $CDCl_3$)

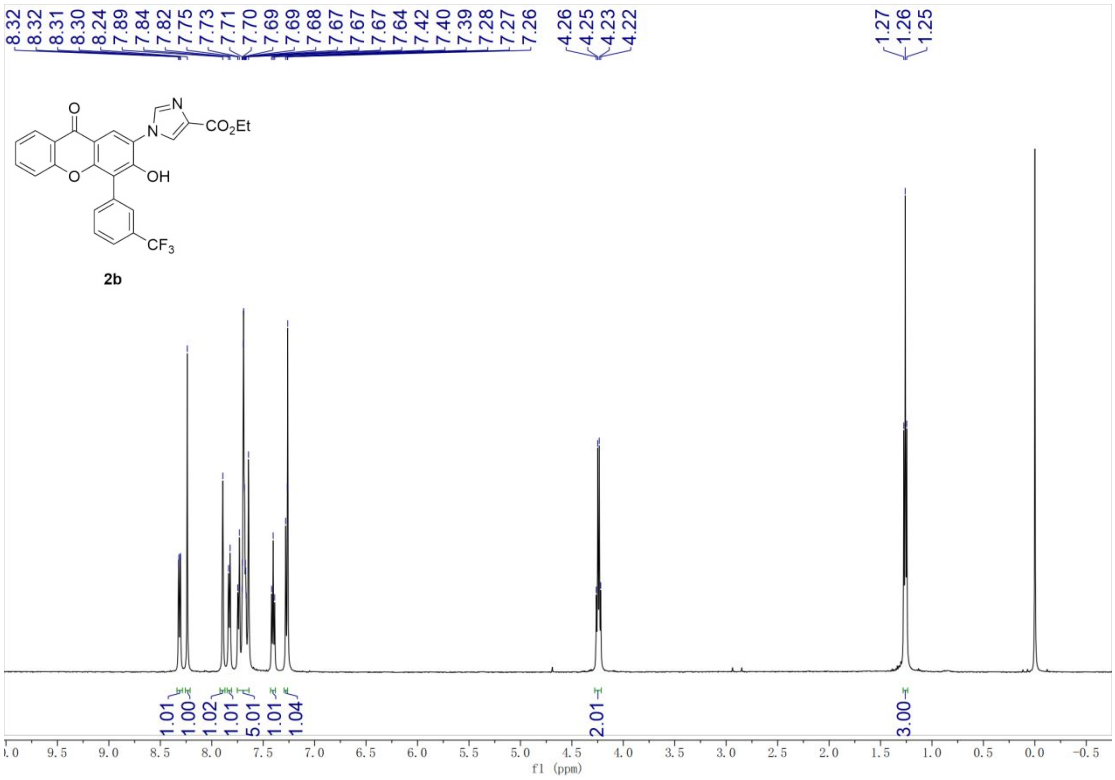



**Figure S8:** $^{1}$H NMR Spectrum of Compound **2b**(500 MHz, $CDCl_3$)

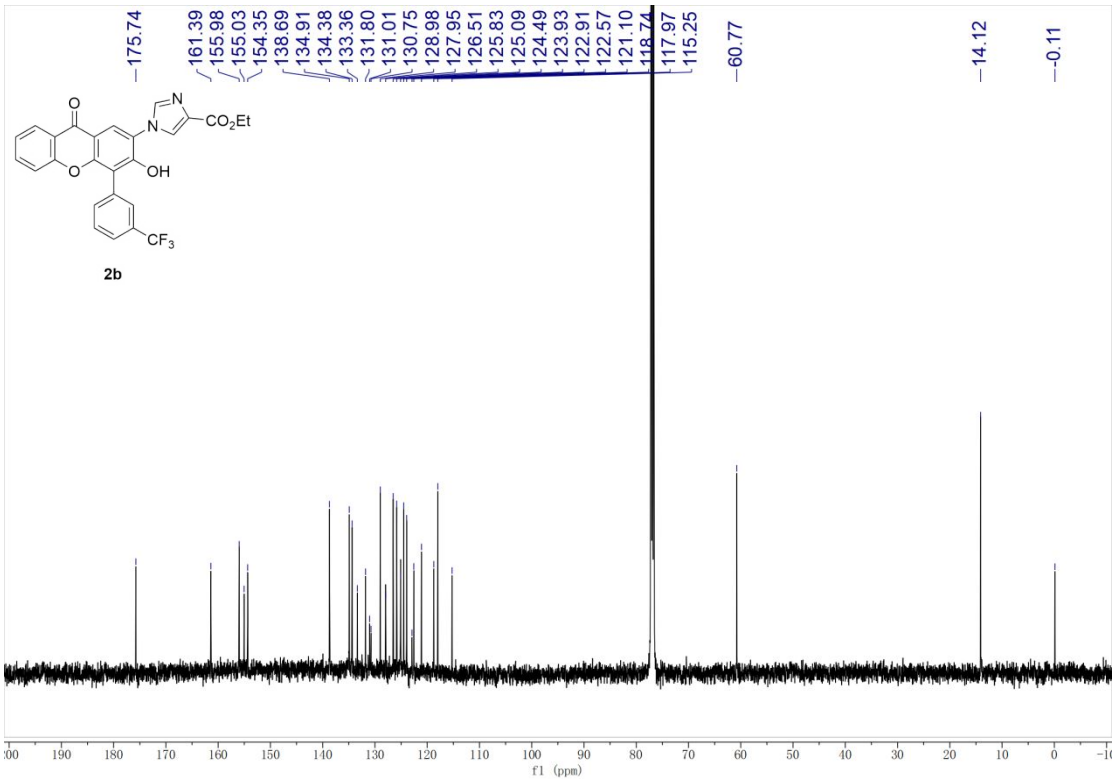



**Figure S9:** $^{13}$C NMR Spectrum of Compound **2b**(125 MHz, $CDCl_3$)

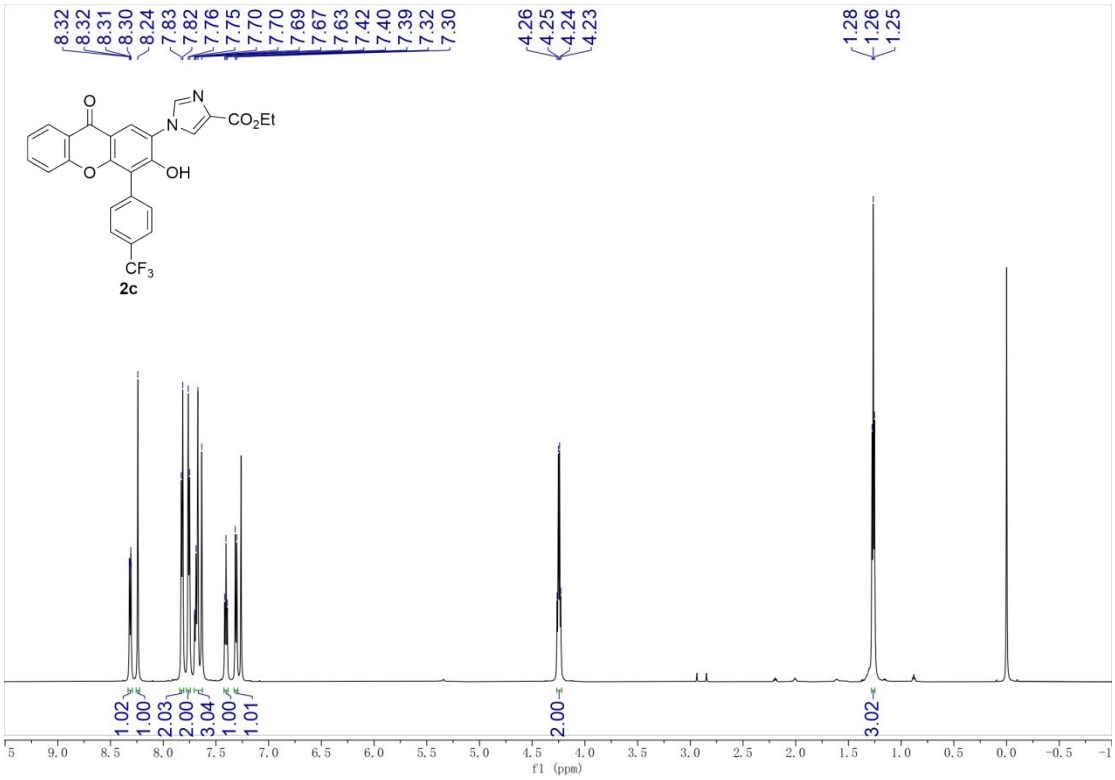



**Figure S10:** $^{1}$H NMR Spectrum of Compound **2c**(600 MHz, $CDCl_3$)

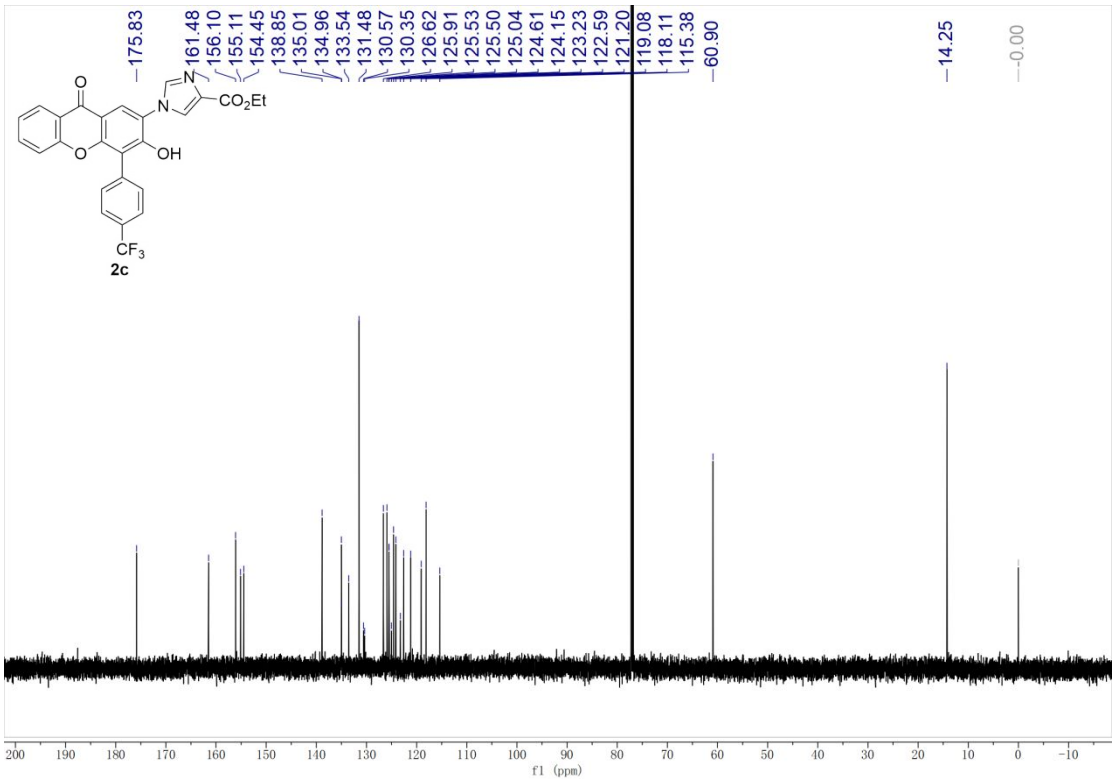



**Figure S11:** $^{13}$C NMR Spectrum of Compound **2c**(150 MHz, $CDCl_3$)

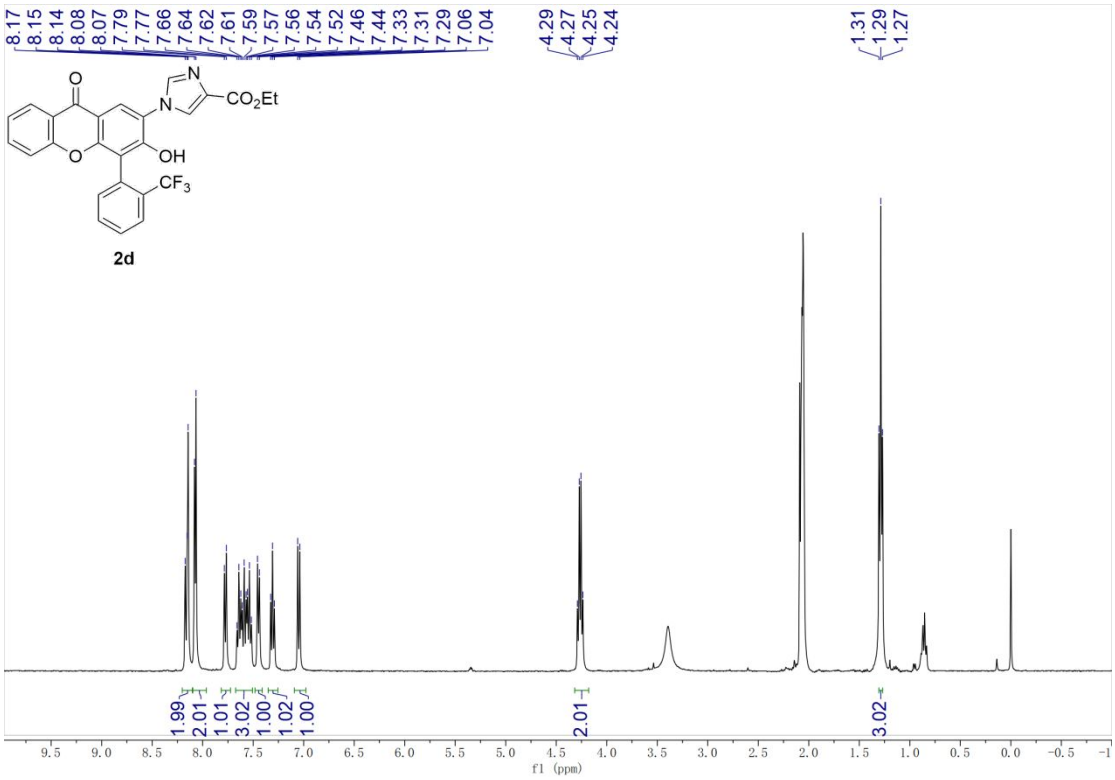



**Figure S12:** [1]H NMR Spectrum of Compound **2d**(400 MHz, Acetone-$d_6$)

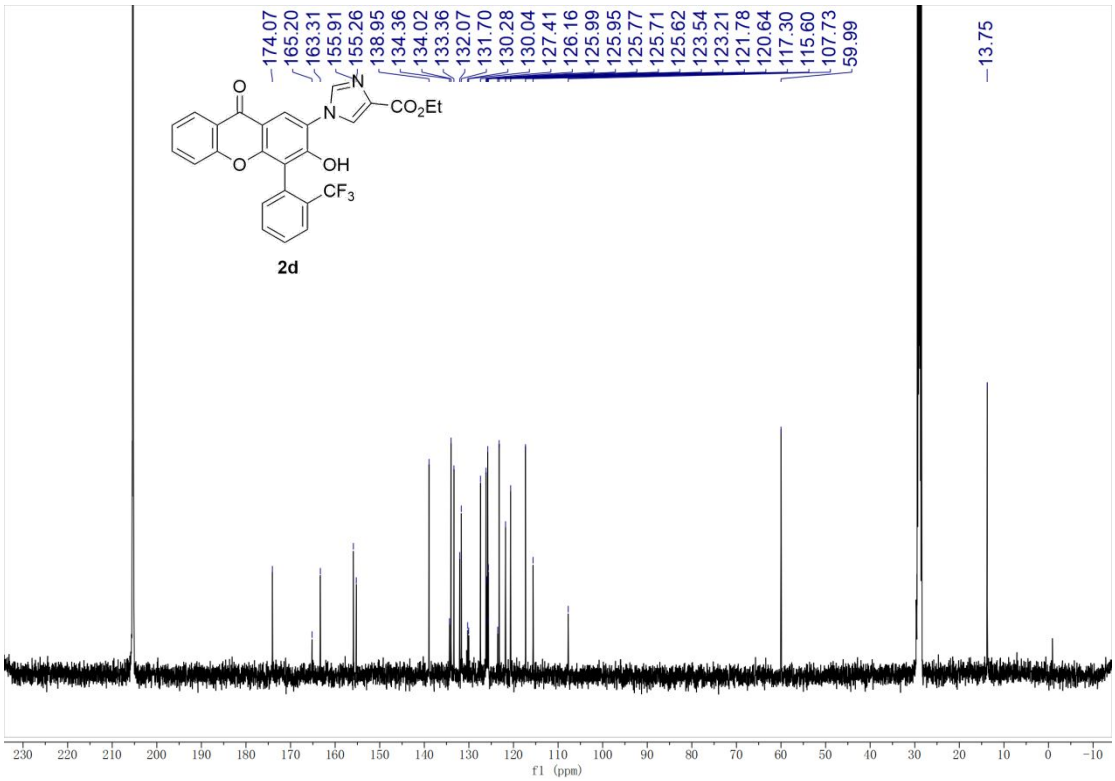



**Figure S13:** [1]H NMR Spectrum of Compound **2d**(125 MHz, Acetone-$d_6$)

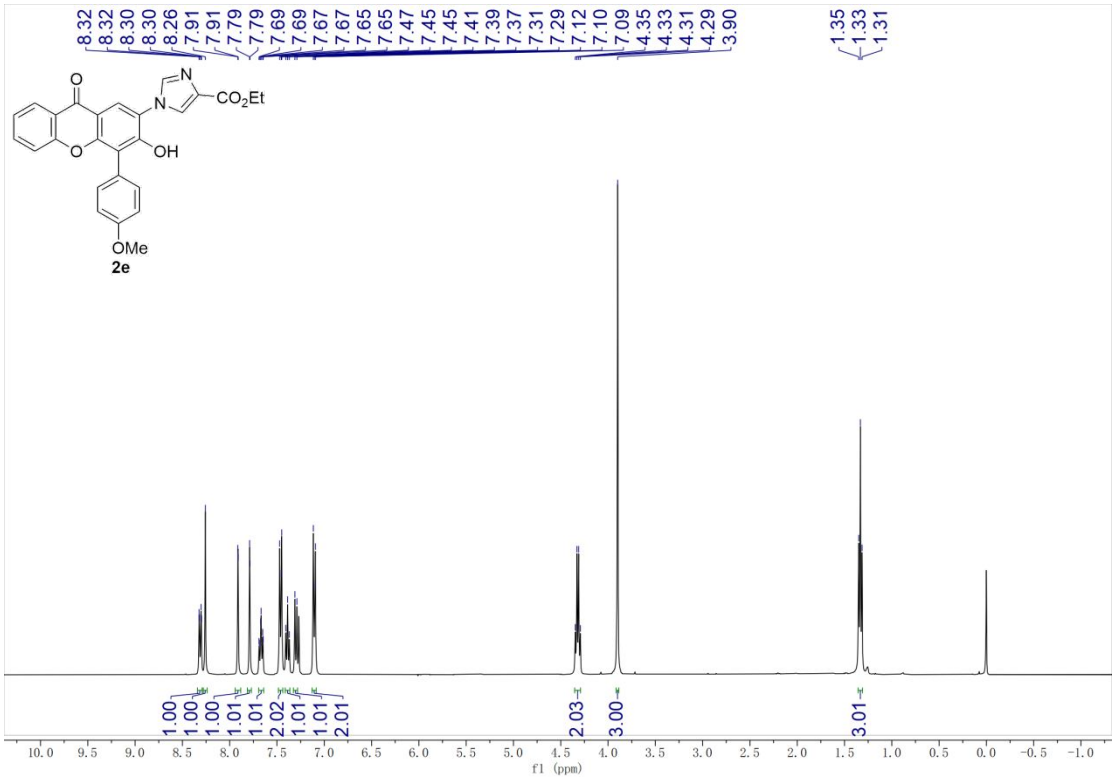



**Figure S14:** $^{1}$H NMR Spectrum of Compound **2e**(400 MHz, $CDCl_3$)

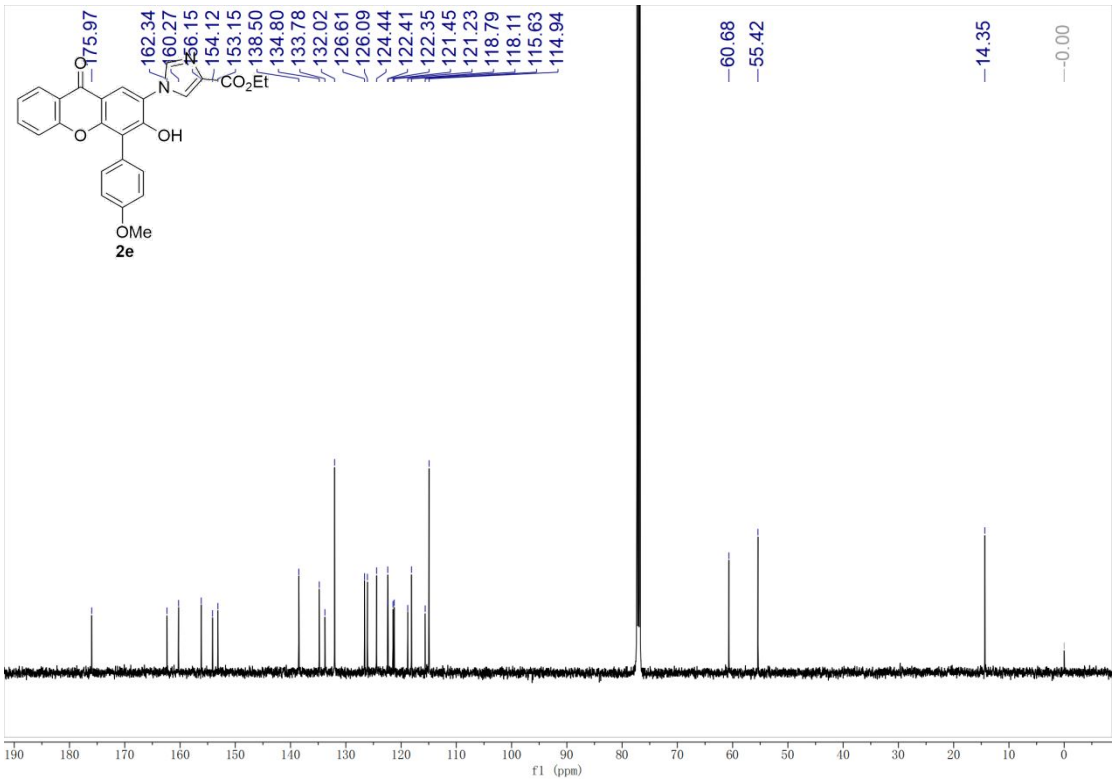



**Figure S15:** $^{13}$C NMR Spectrum of Compound **2e**(125 MHz, $CDCl_3$)

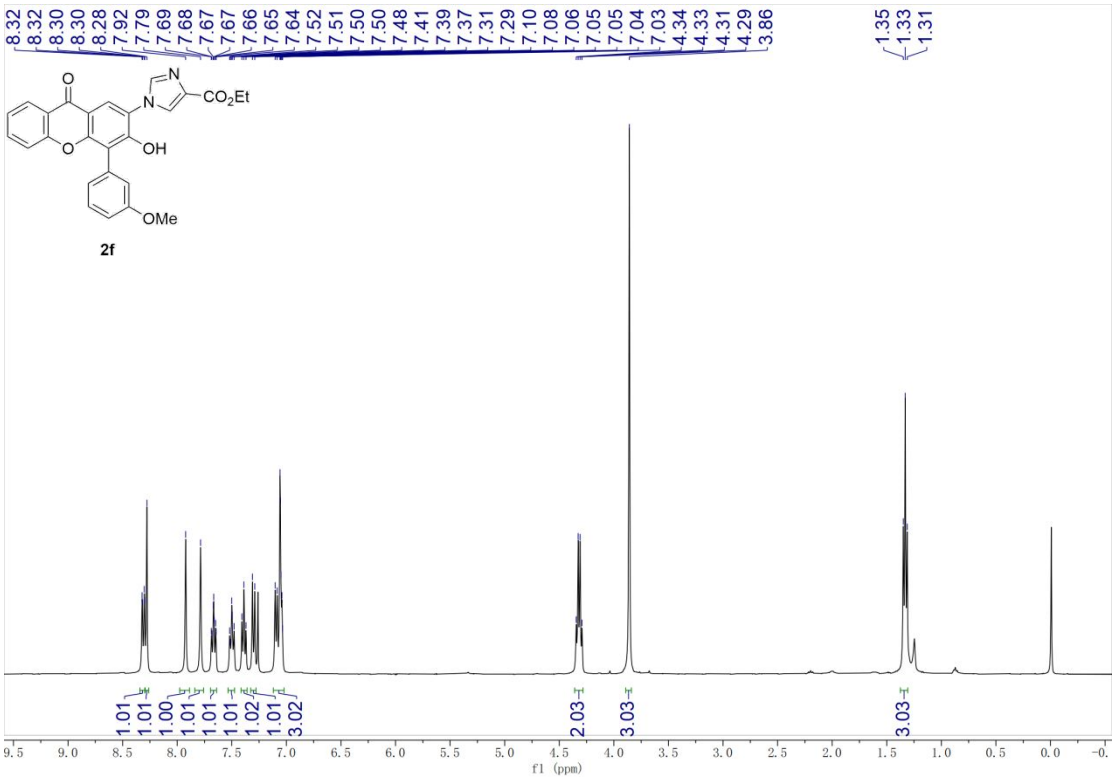



**Figure S16:** $^{1}$H NMR Spectrum of Compound **2f**(400 MHz, $CDCl_3$)

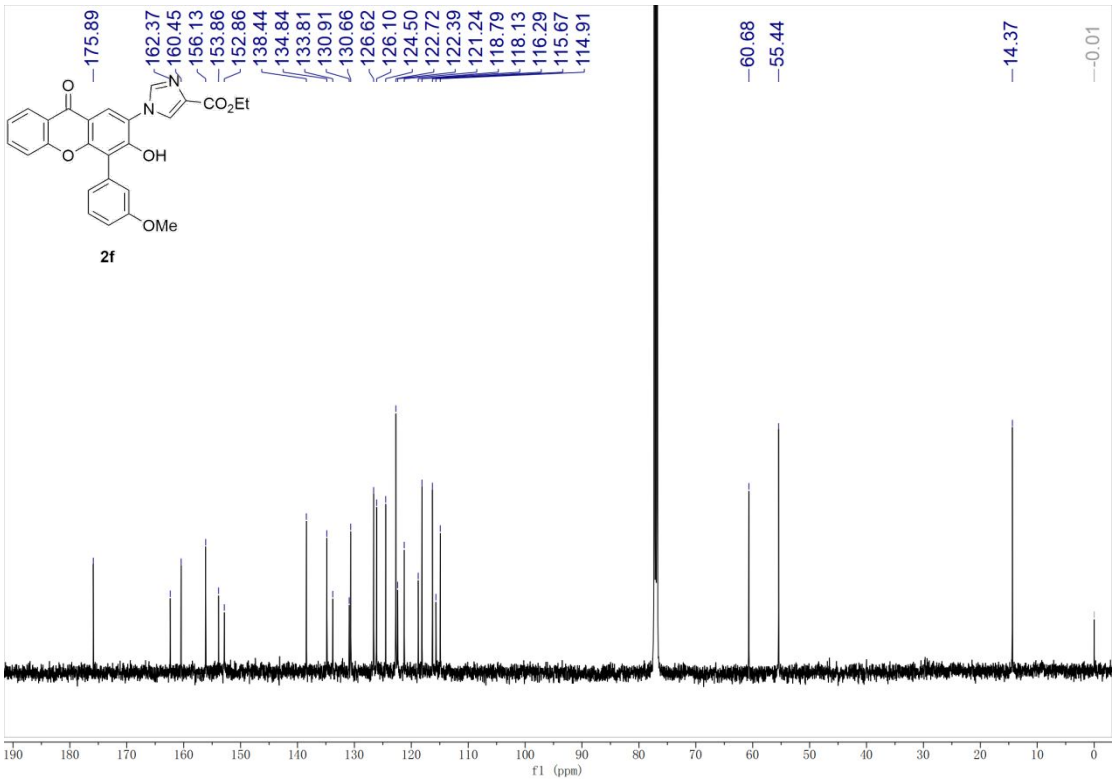



**Figure S17:** $^{13}$C NMR Spectrum of Compound **2f**(125 MHz, $CDCl_3$)

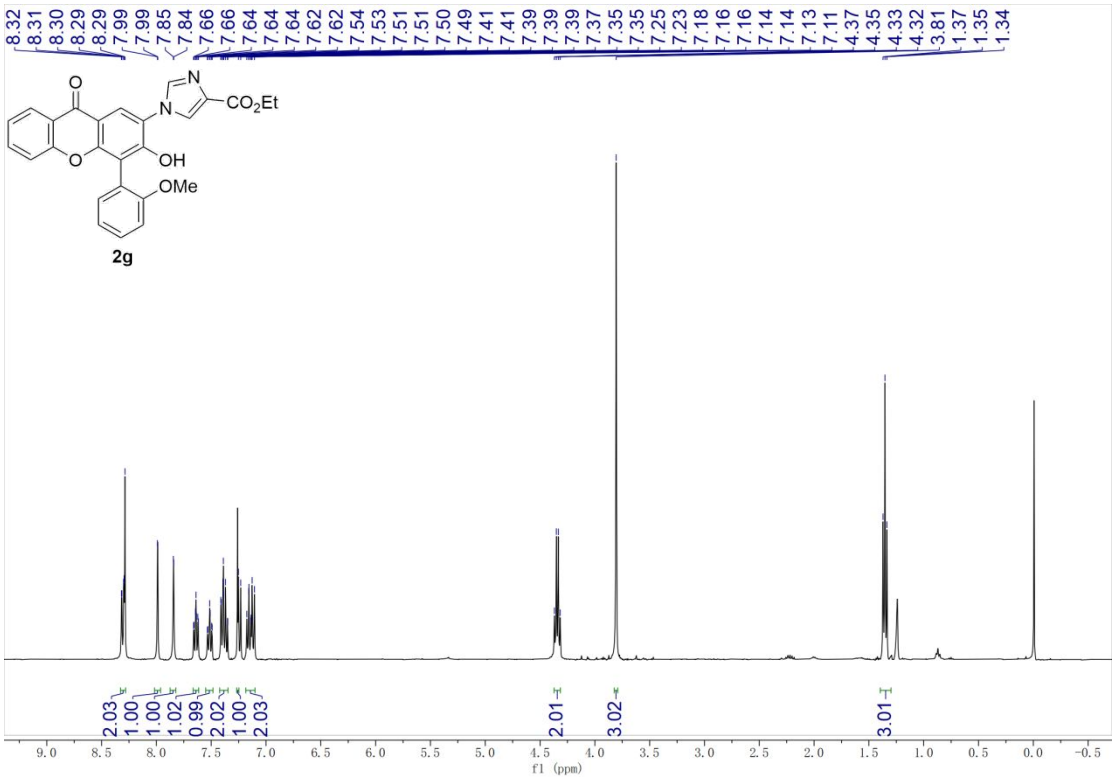



**Figure S18:** $^{1}$H NMR Spectrum of Compound **2g**(400 MHz, $CDCl_3$)

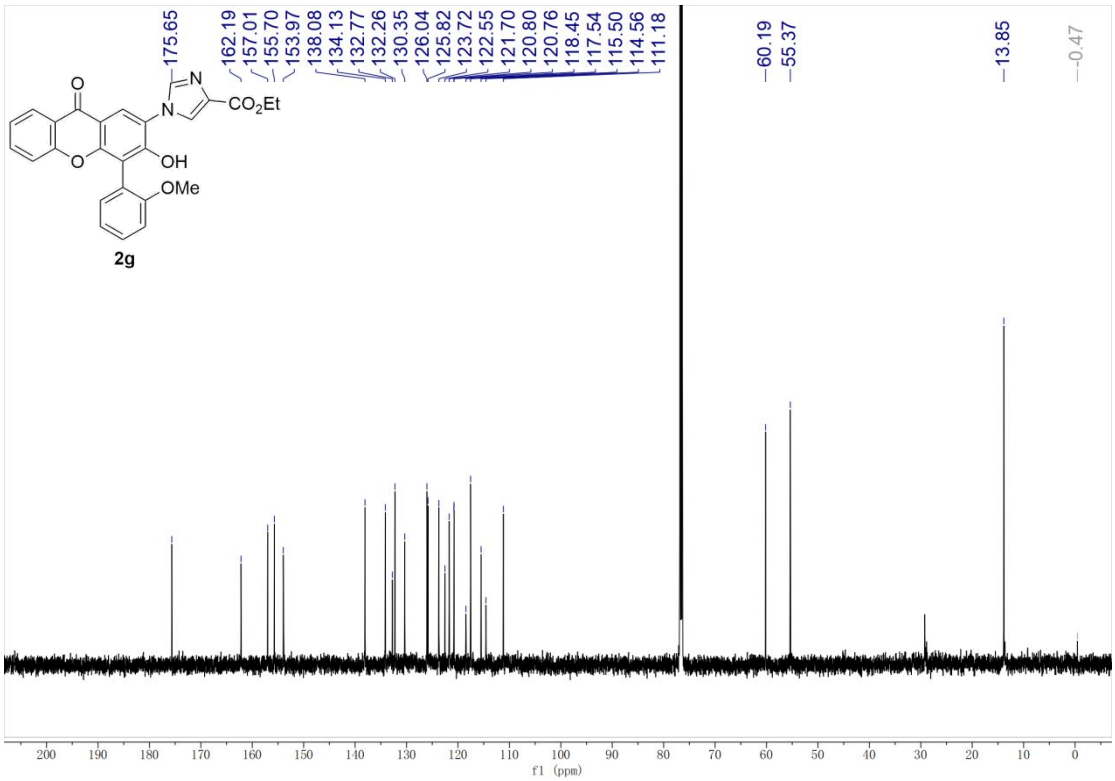



**Figure S19:** $^{13}$C NMR Spectrum of Compound **2g**(150 MHz, $CDCl_3$)

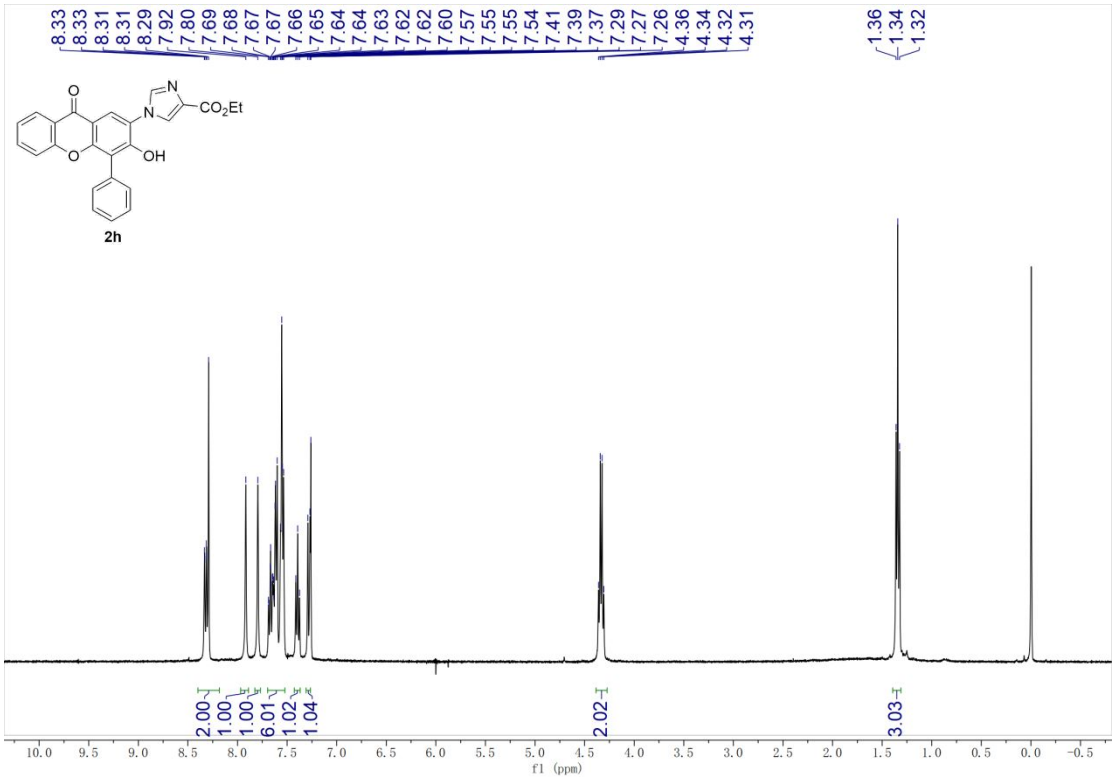



**Figure S20:** $^{1}$H NMR Spectrum of Compound **2h**(400 MHz, $CDCl_3$)

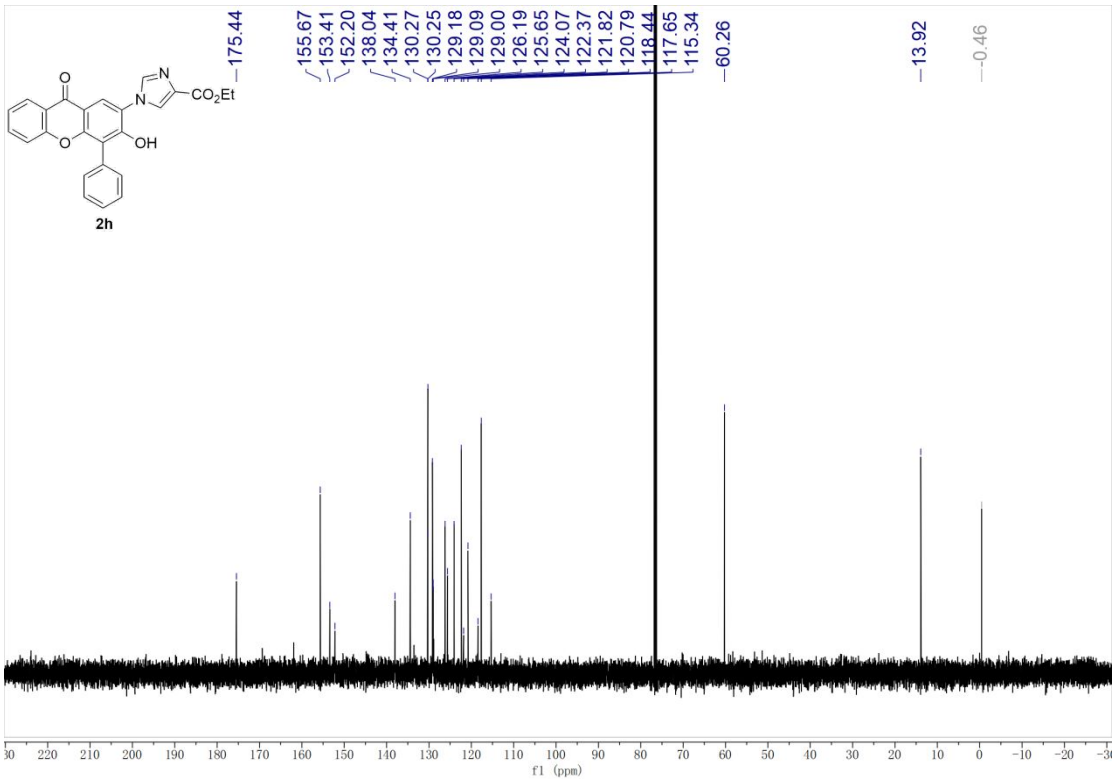



**Figure S21:** $^{13}$C NMR Spectrum of Compound **2h**(125 MHz, $CDCl_3$)

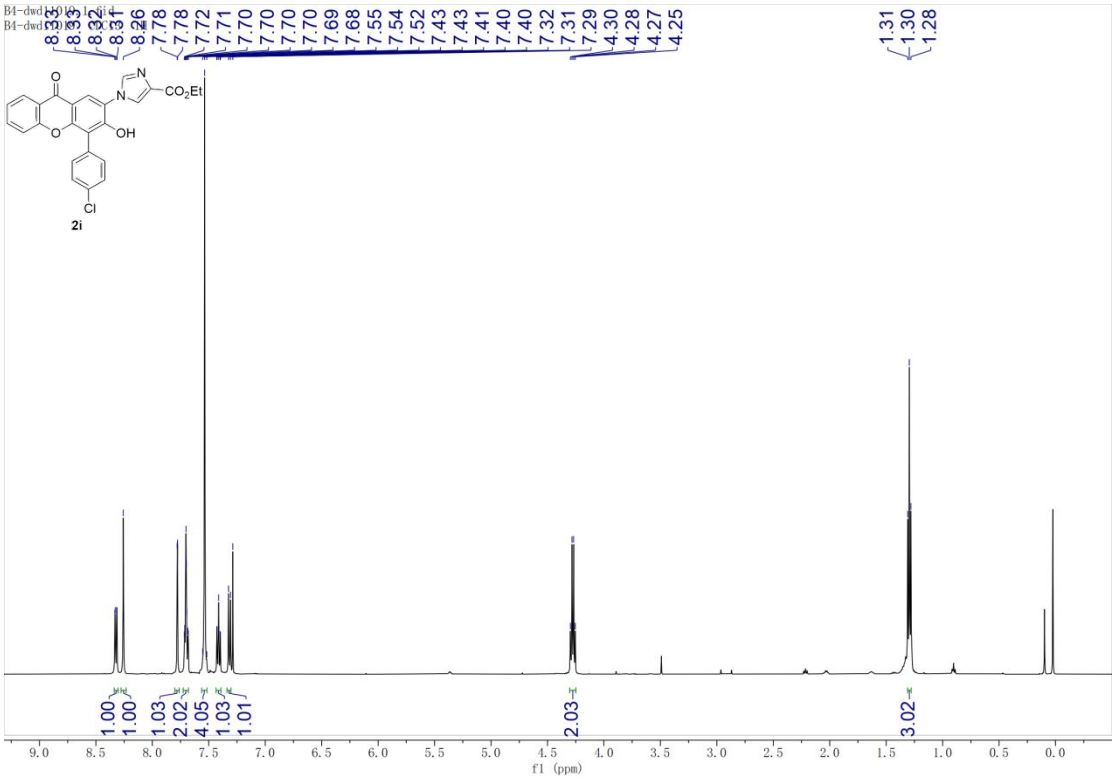



**Figure S22:** $^{1}$H NMR Spectrum of Compound **2i**(500 MHz, $CDCl_3$)

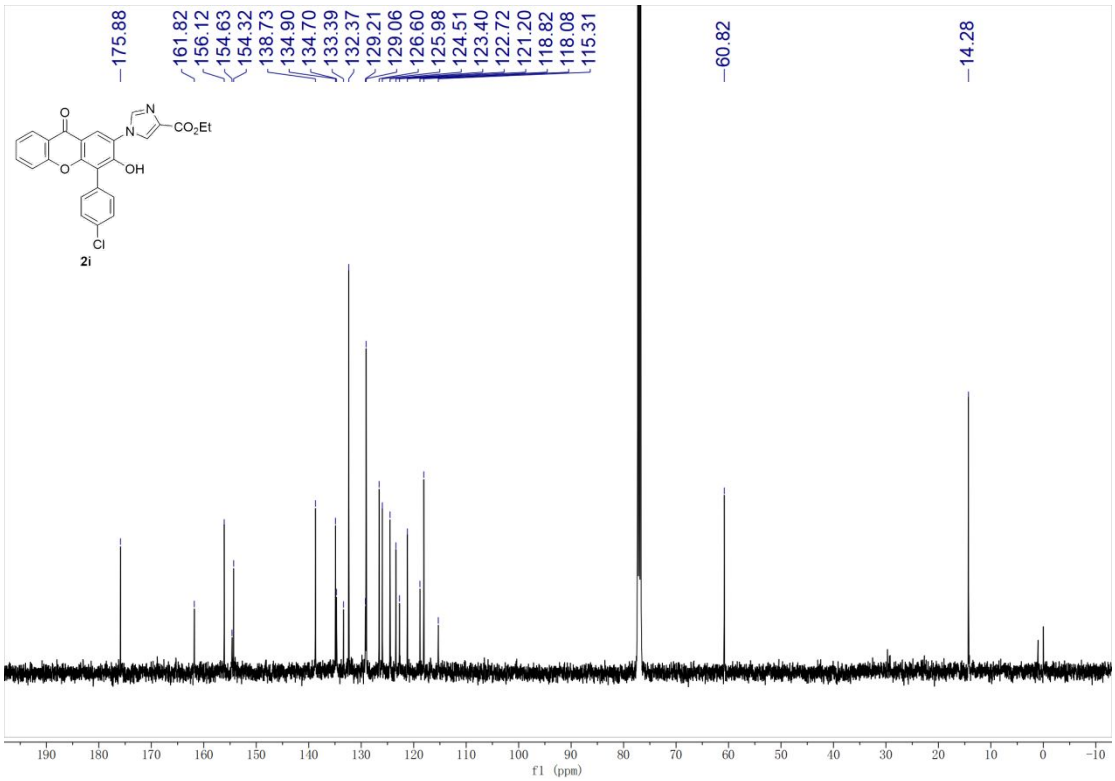



**Figure S23:** $^{13}$C NMR Spectrum of Compound **2i**(125 MHz, $CDCl_3$)

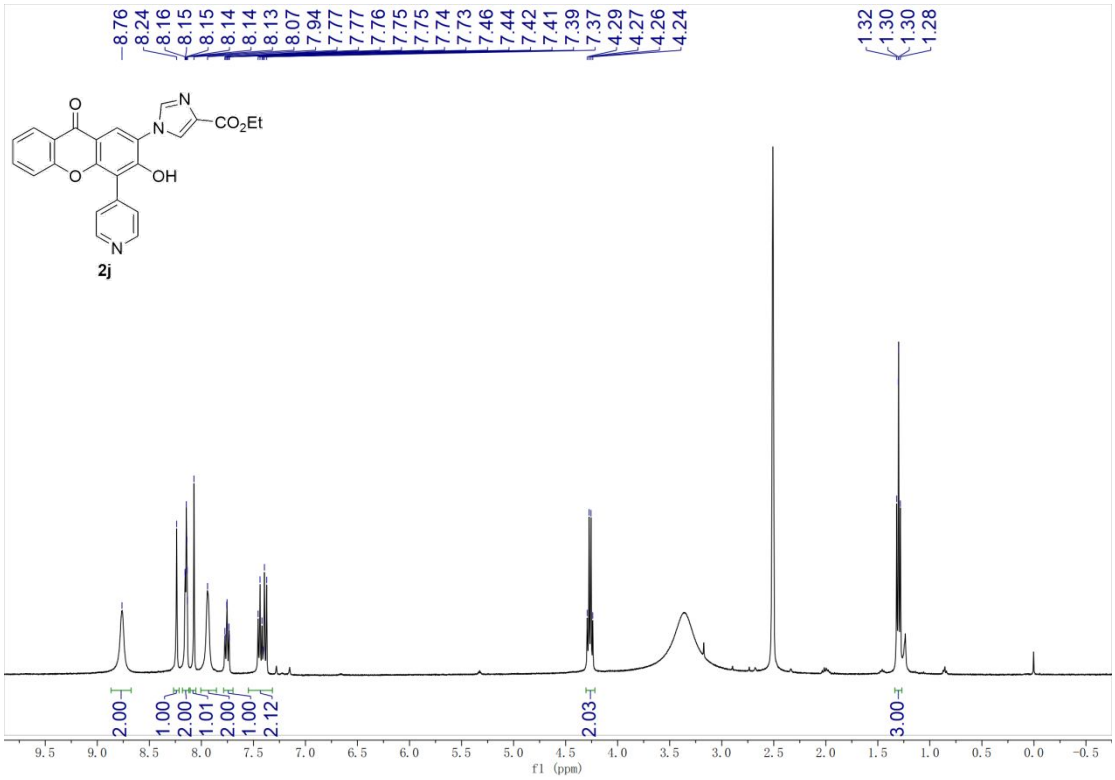



**Figure S24:** $^{1}$H NMR Spectrum of Compound **2j**(400 MHz, DMSO-$d_6$)

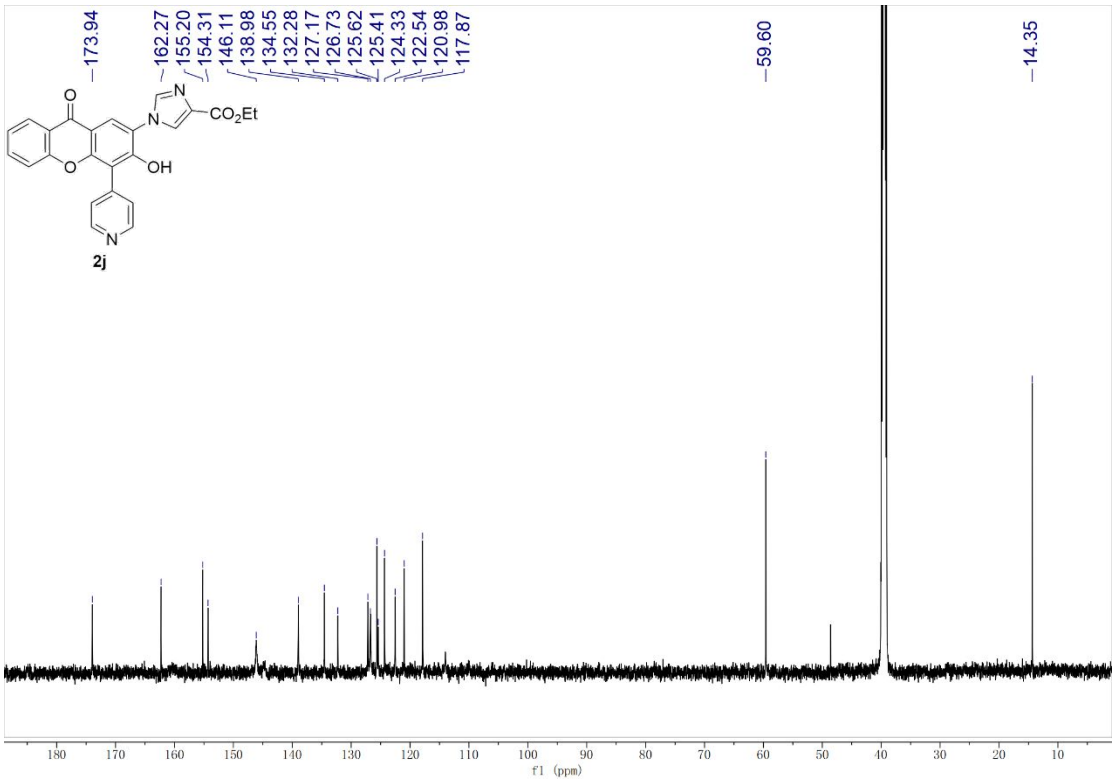



**Figure S25:** $^{13}$C NMR Spectrum of Compound **2j**(150 MHz, 1:20 v/v $CD_3OD$ in DMSO-$d_6$)

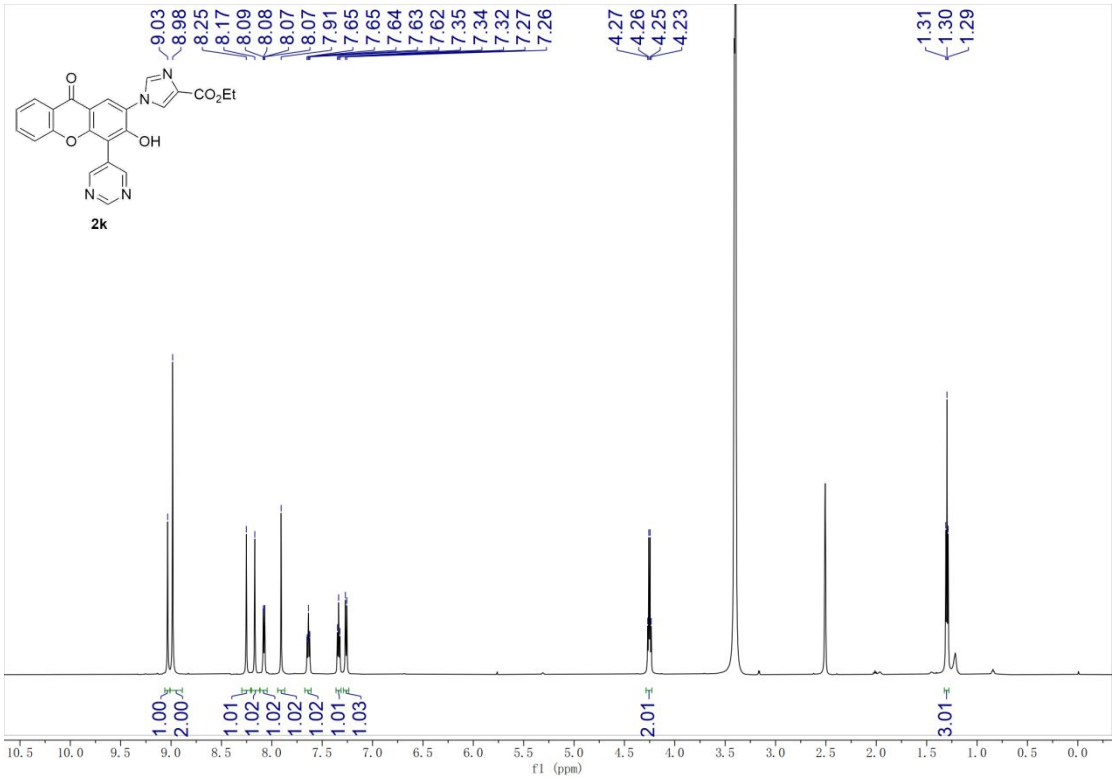



**Figure S26:** $^{1}$H NMR Spectrum of Compound **2k**(600 MHz, DMSO-$d_6$)

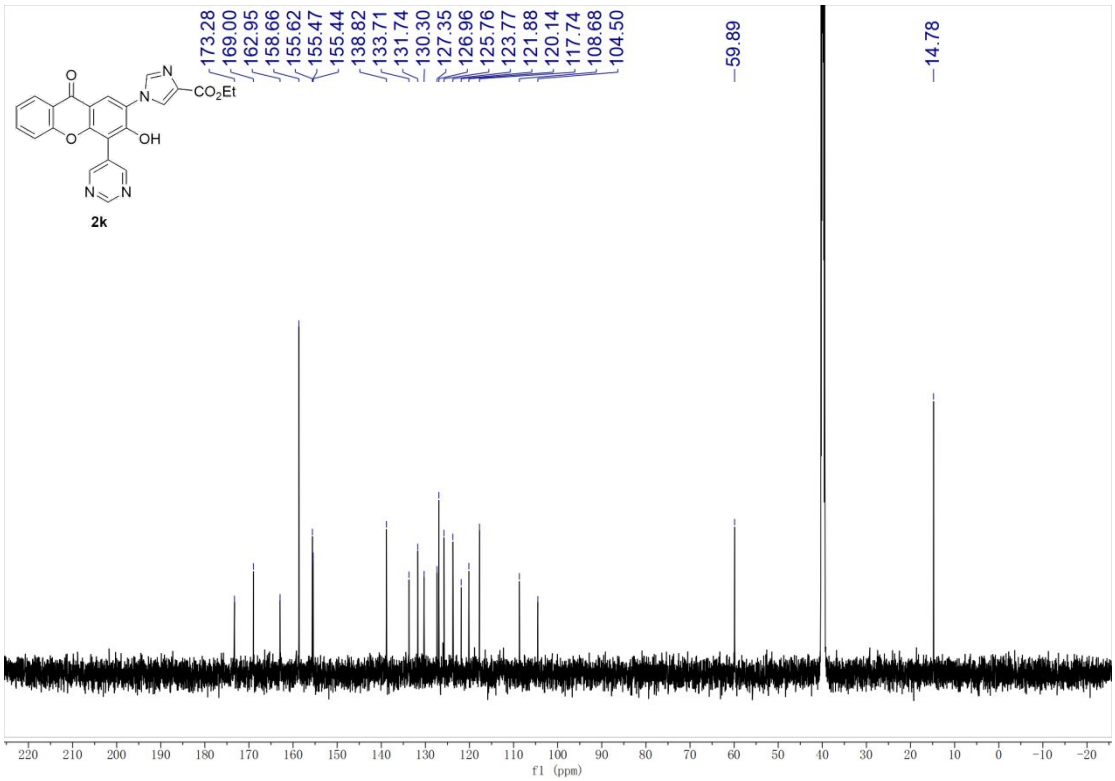



**Figure S27:** $^{13}$C NMR Spectrum of Compound **2k**(150 MHz, DMSO-$d_6$)

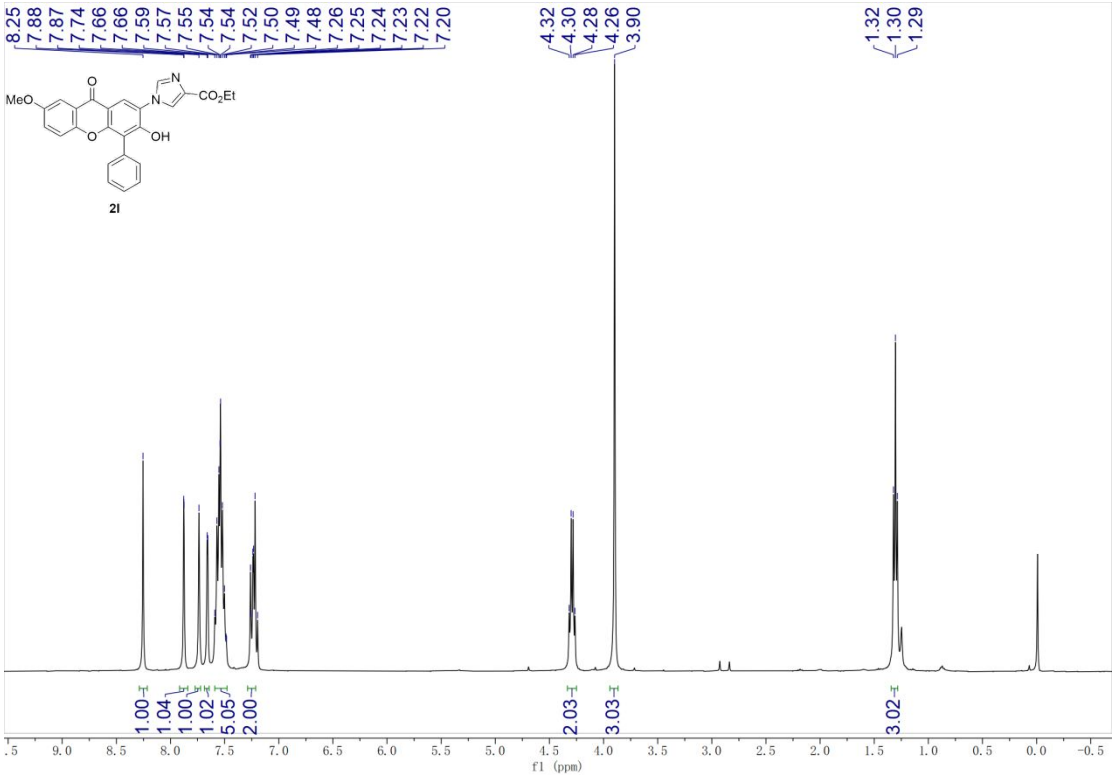



**Figure S28:** $^{1}$H NMR Spectrum of Compound **2l**(400 MHz, $CDCl_3$)

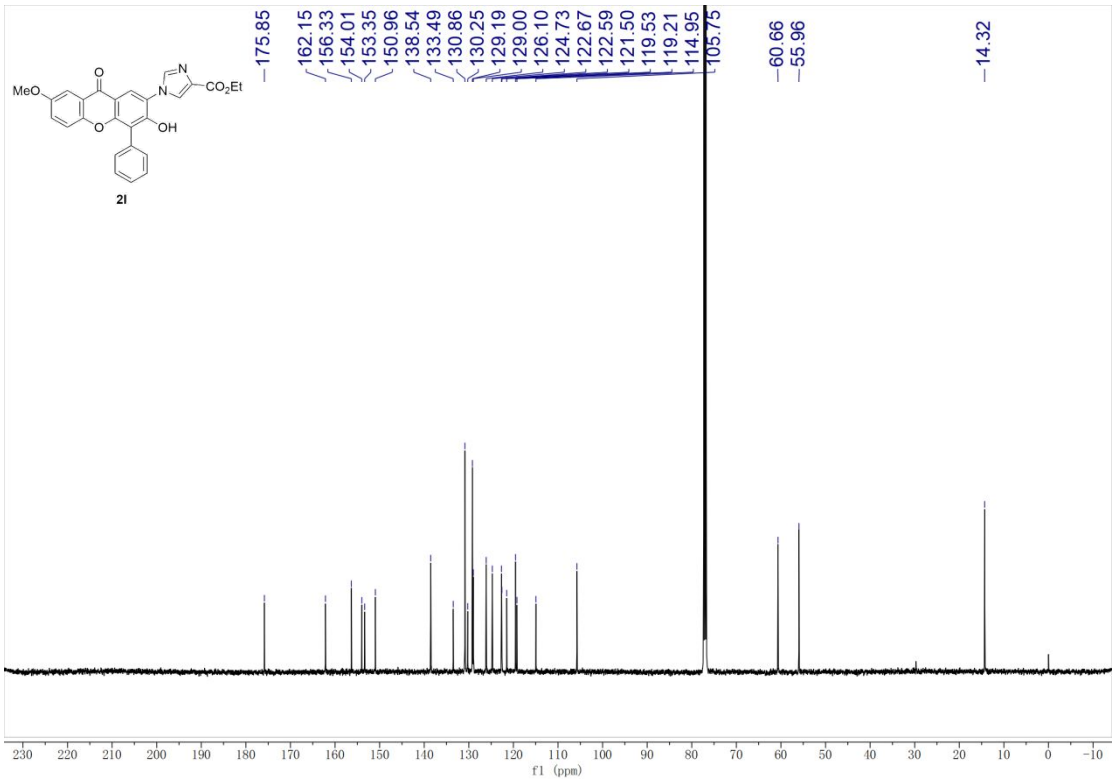



**Figure S29:** $^{13}$C NMR Spectrum of Compound **2l**(125 MHz, $CDCl_3$)

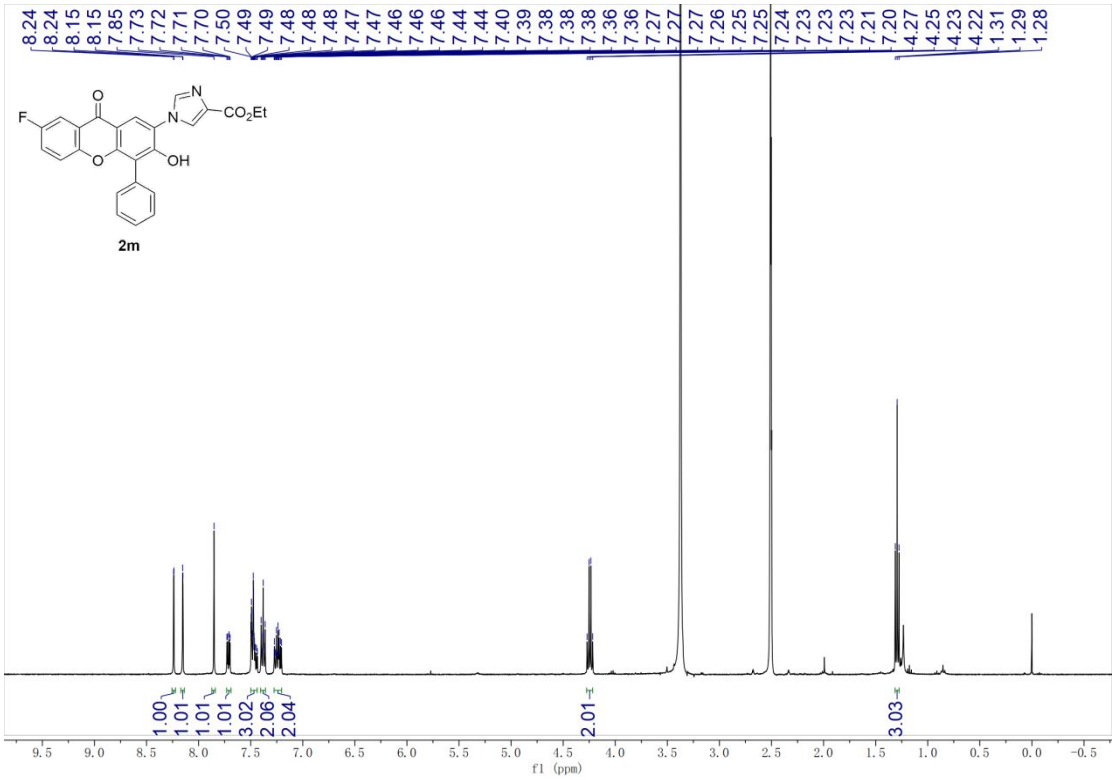



**Figure S30:** $^{1}$H NMR Spectrum of Compound **2m**(400 MHz, DMSO-$d_6$)

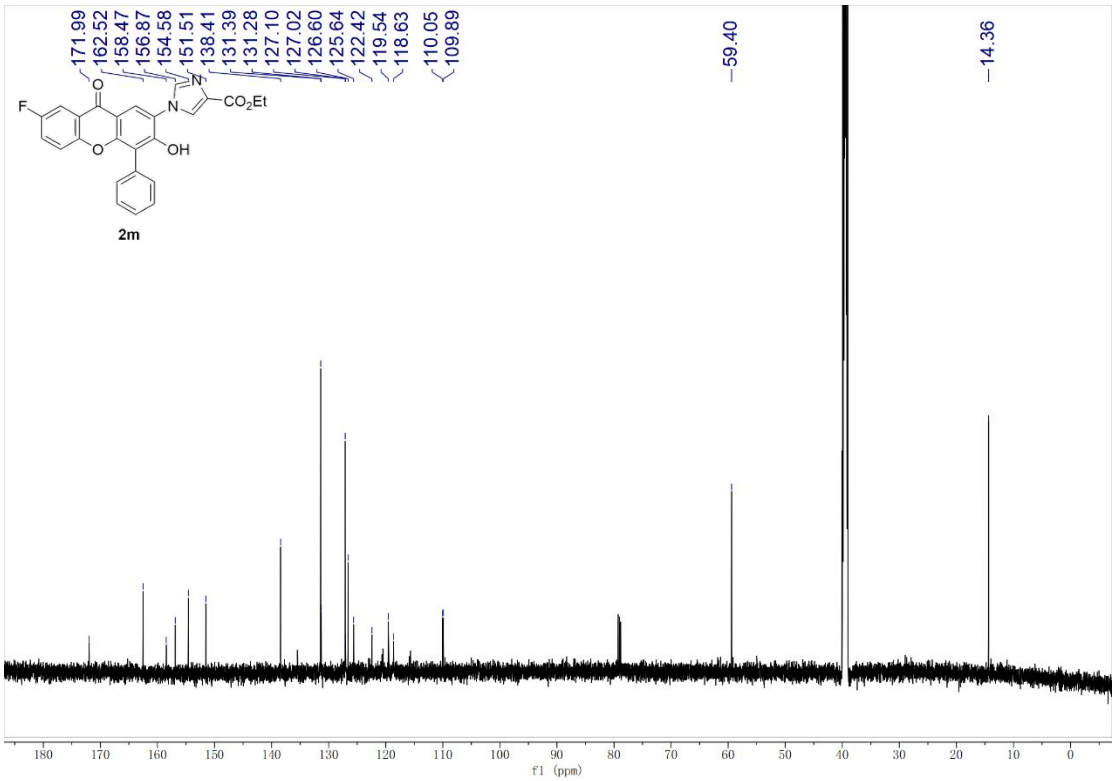



**Figure S31:** $^{13}$C NMR Spectrum of Compound **2m**(150 MHz, DMSO-$d_6$)

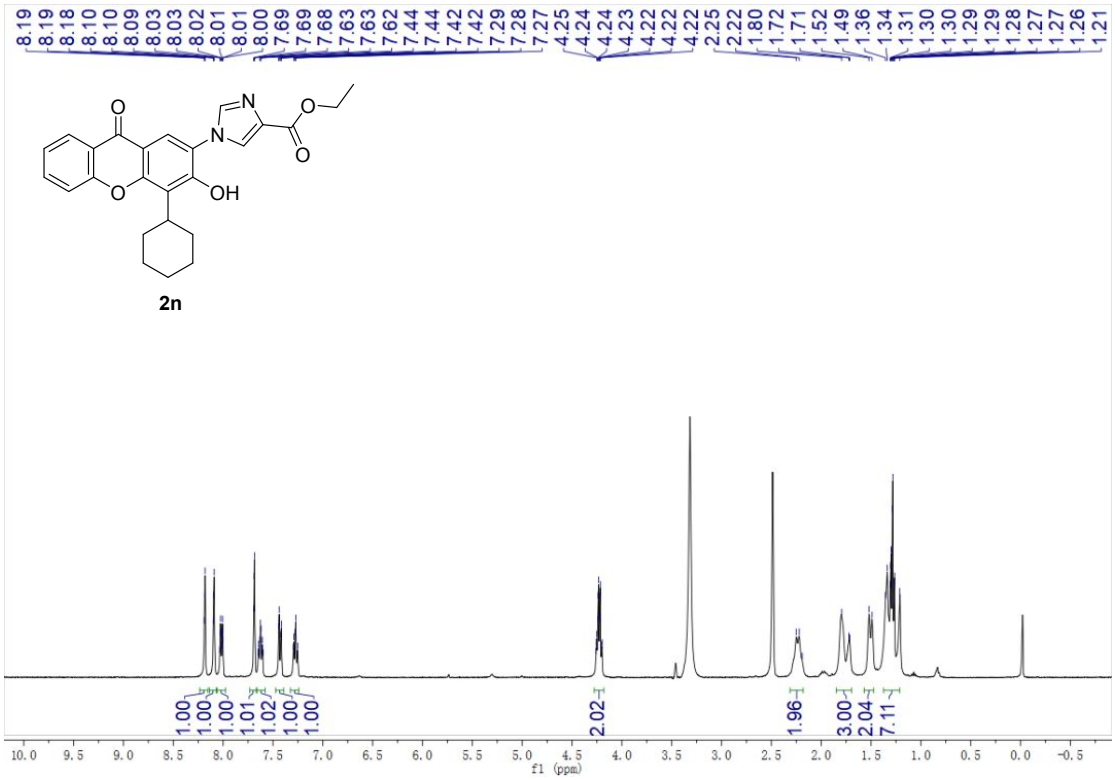



**Figure S32:** $^{1}$H NMR Spectrum of Compound **2n**(400 MHz, DMSO-$d_6$)

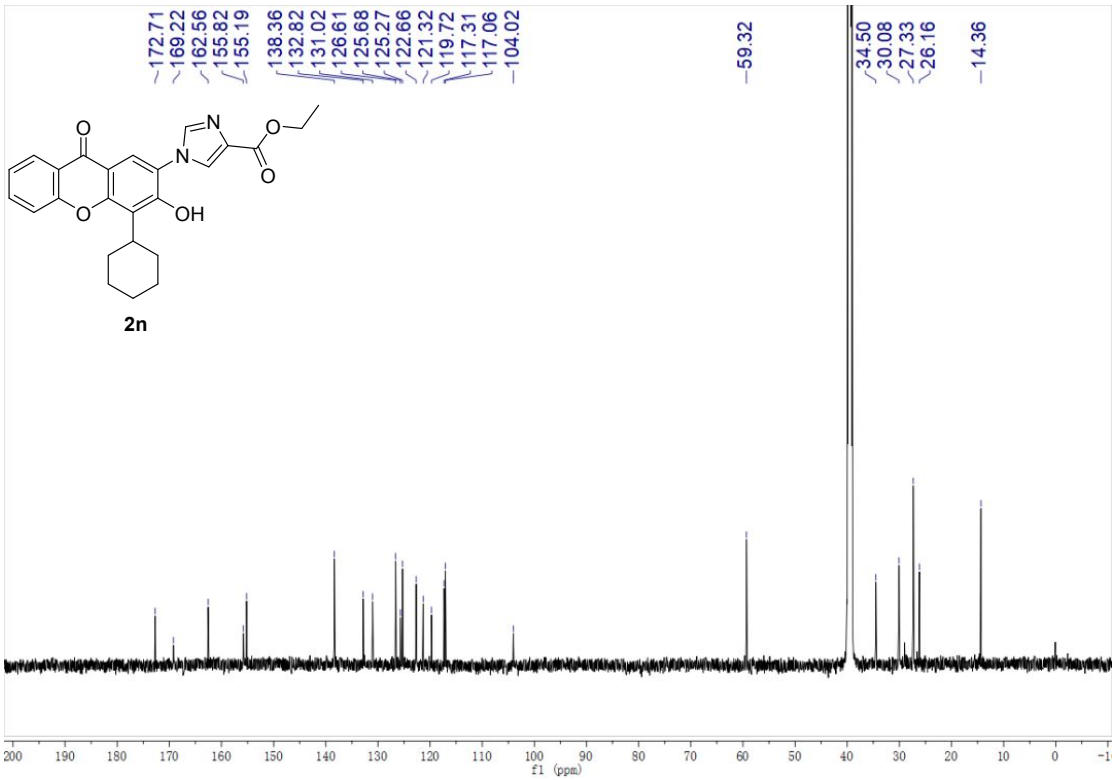



**Figure S33:** $^{13}$C NMR Spectrum of Compound **2n**(150 MHz, DMSO-$d_6$)

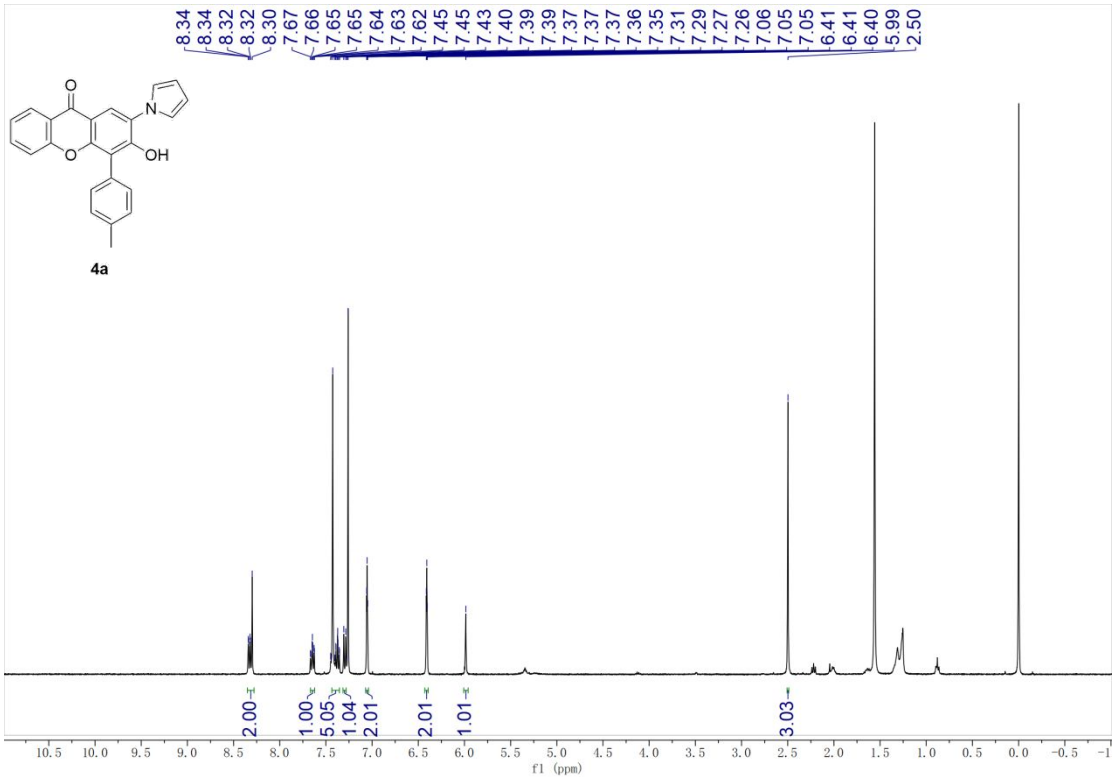



**Figure S34:** $^{1}$H NMR Spectrum of Compound **4a**(500 MHz, $CDCl_3$)

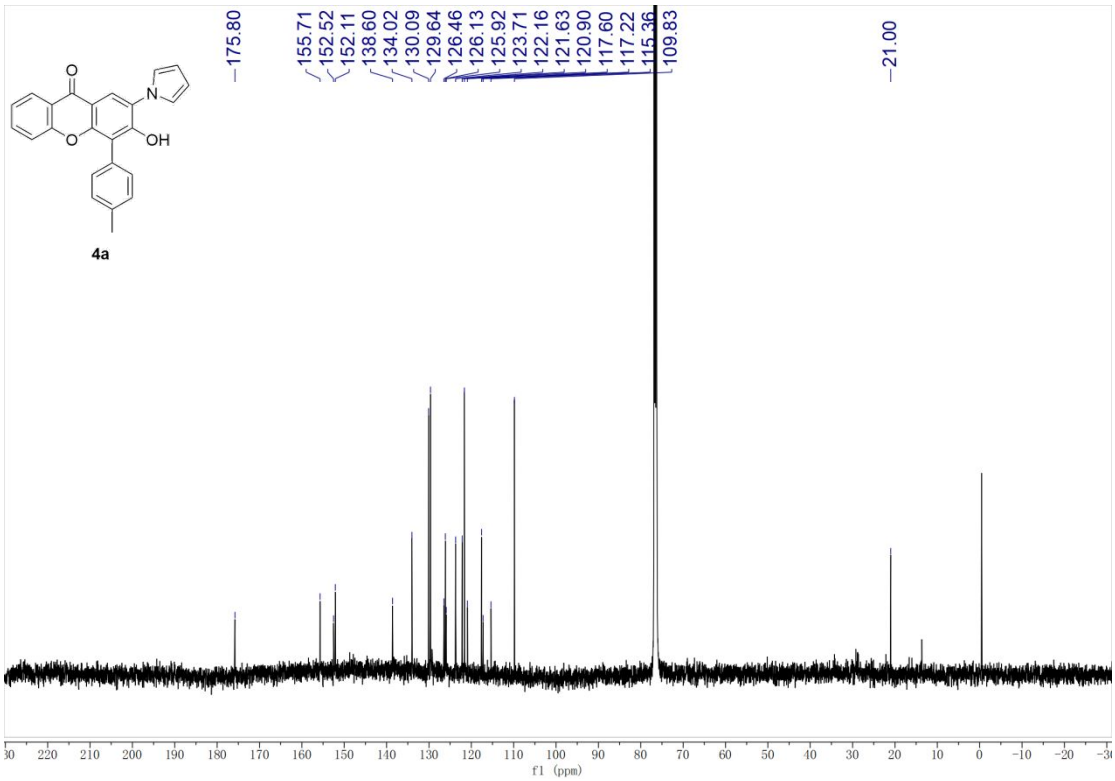



**Figure S35:** $^{13}$C NMR Spectrum of Compound **4a**(125 MHz, $CDCl_3$)

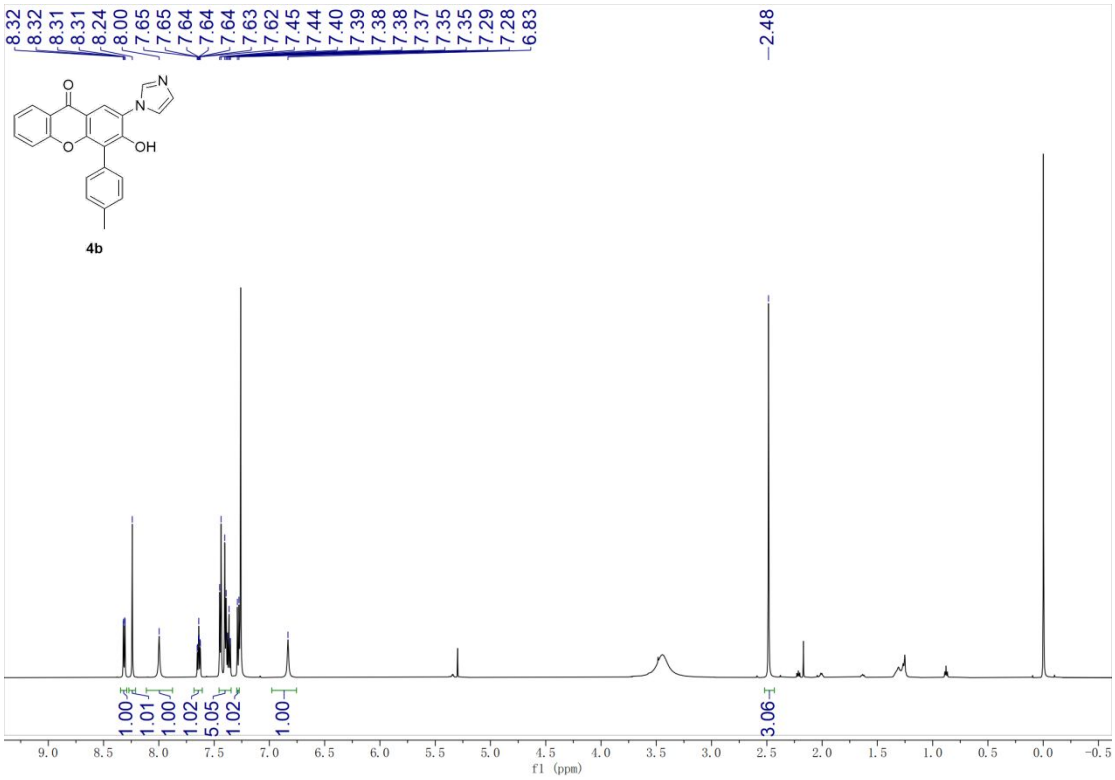



**Figure S36:** $^{1}$H NMR Spectrum of Compound **4b**(600 MHz, $CDCl_3$)

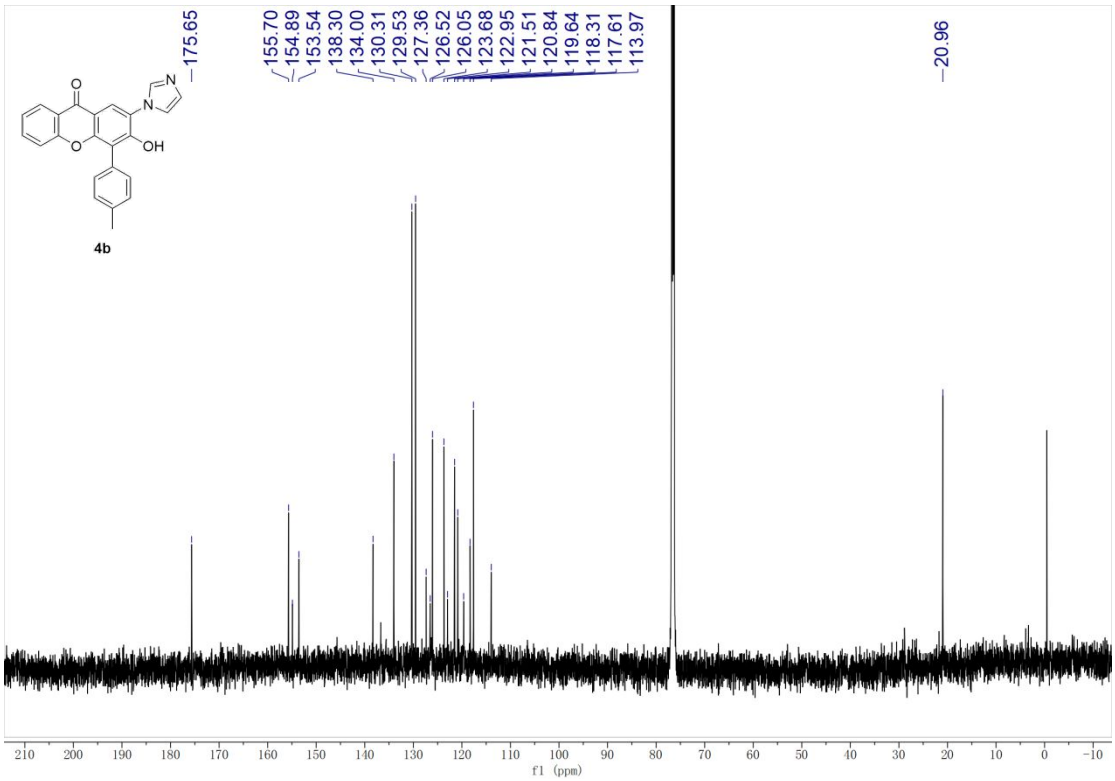



**Figure S37:** $^{13}$C NMR Spectrum of Compound **4b**(150 MHz, $CDCl_3$)

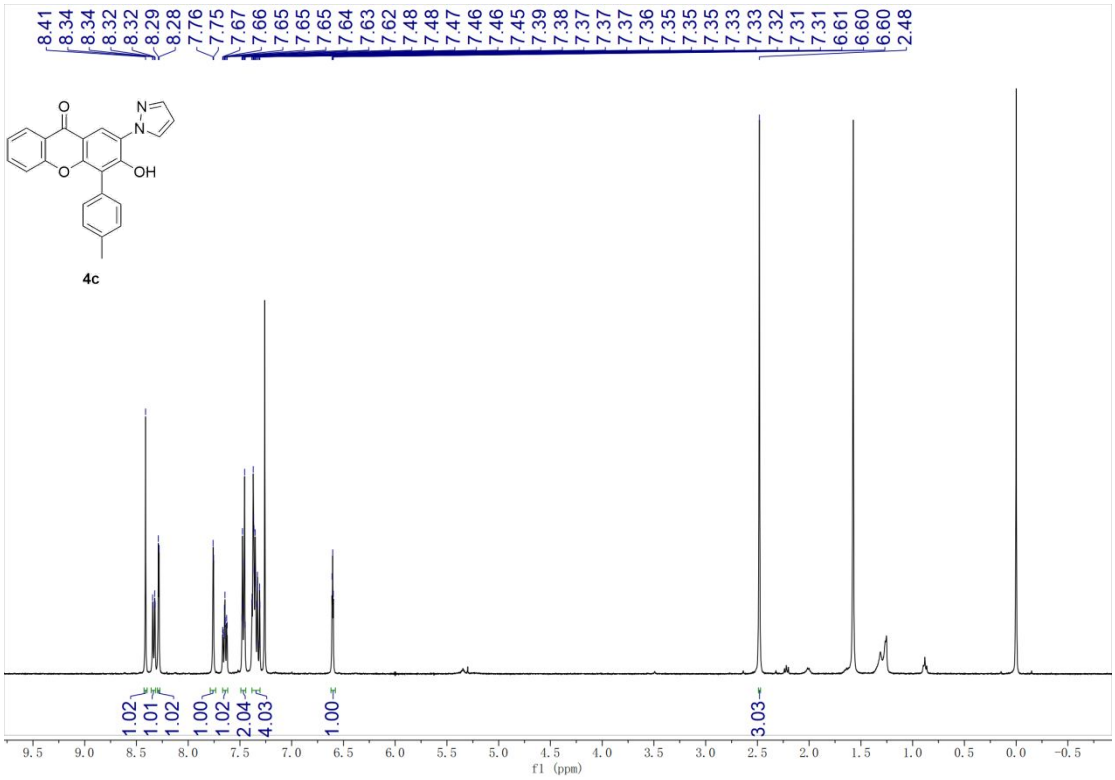



**Figure S38:** $^{1}$H NMR Spectrum of Compound **4c**(400 MHz, $CDCl_3$)

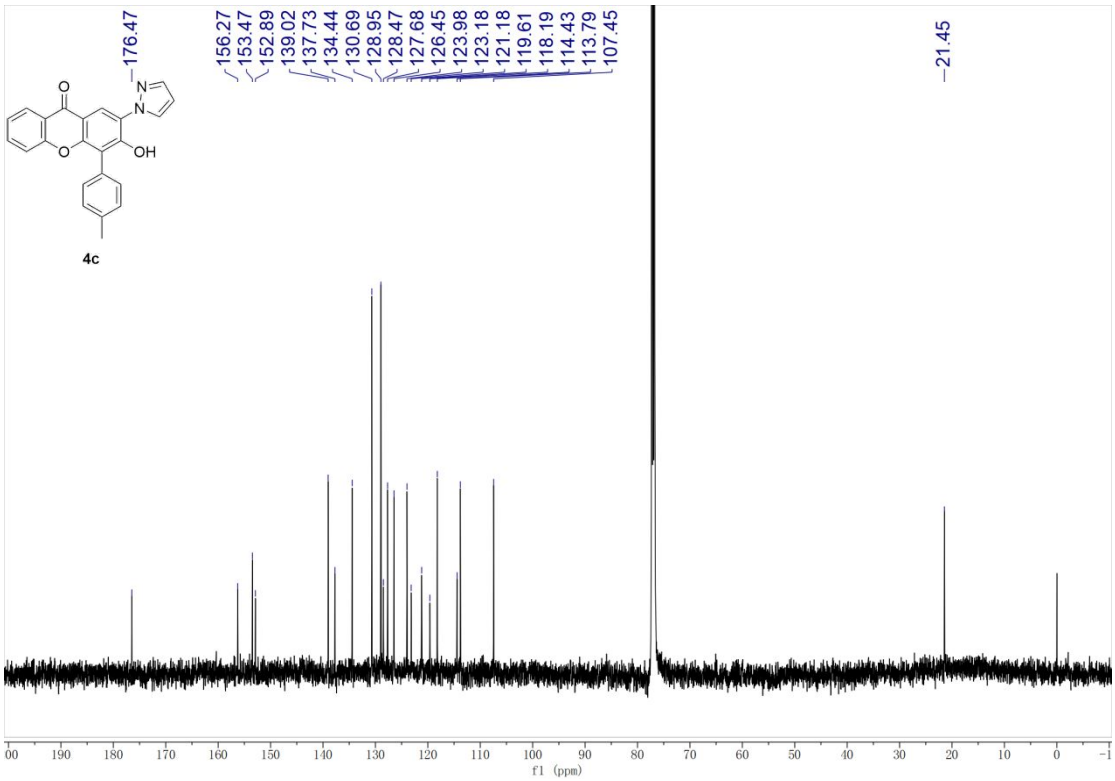



**Figure S39:** $^{13}$C NMR Spectrum of Compound **4c**(125 MHz, $CDCl_3$)

3. X-ray Crystallography data of compound **2i**

Compound **2i** was recrystallized in mixed solvent of hexane and dichloromethane.
CCDC 1987456 **(2i)** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

**Table S2** Crystal refinement data of compound **2i**

| | |
|---|---|
| Empirical formula | $C_{28}H_{24}ClN_2O_5$ |
| Formula weight | 503.94 |
| Temperature/K | 110.0 |
| Crystal system | tetragonal |
| Space group | P4/n |
| a/Å | 26.429(2) |
| b/Å | 26.429(2) |
| c/Å | 7.8670(7) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| Volume/Å$^3$ | 5495.1(11) |
| Z | 8 |
| $\rho_{calc}$g/cm$^3$ | 1.218 |
| μ/mm$^{-1}$ | 0.177 |
| F(000) | 2104.0 |
| Crystal size/mm$^3$ | 0.12 × 0.08 × 0.05 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 4.36 to 50.018 |
| Index ranges | -31 ≤ h ≤ 31, -28 ≤ k ≤ 27, -9 ≤ l ≤ 8 |
| Reflections collected | 18173 |
| Independent reflections | 4844 [$R_{int}$ = 0.1201, $R_{sigma}$ = 0.1197] |
| Data/restraints/parameters | 4844/0/328 |
| Goodness-of-fit on F$^2$ | 1.048 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0746, $wR_2$ = 0.1877 |
| Final R indexes [all data] | $R_1$ = 0.1561, $wR_2$ = 0.2393 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.57/-0.41 |