

### Supplementary Information

## **Novel quinoline-fused quinolone derivatives: synthesis, photophysical studies, solvatochromism and chemosensing applications toward Cu<sup>2+</sup>, Fe<sup>3+</sup>, and Hg<sup>2+</sup> ions**

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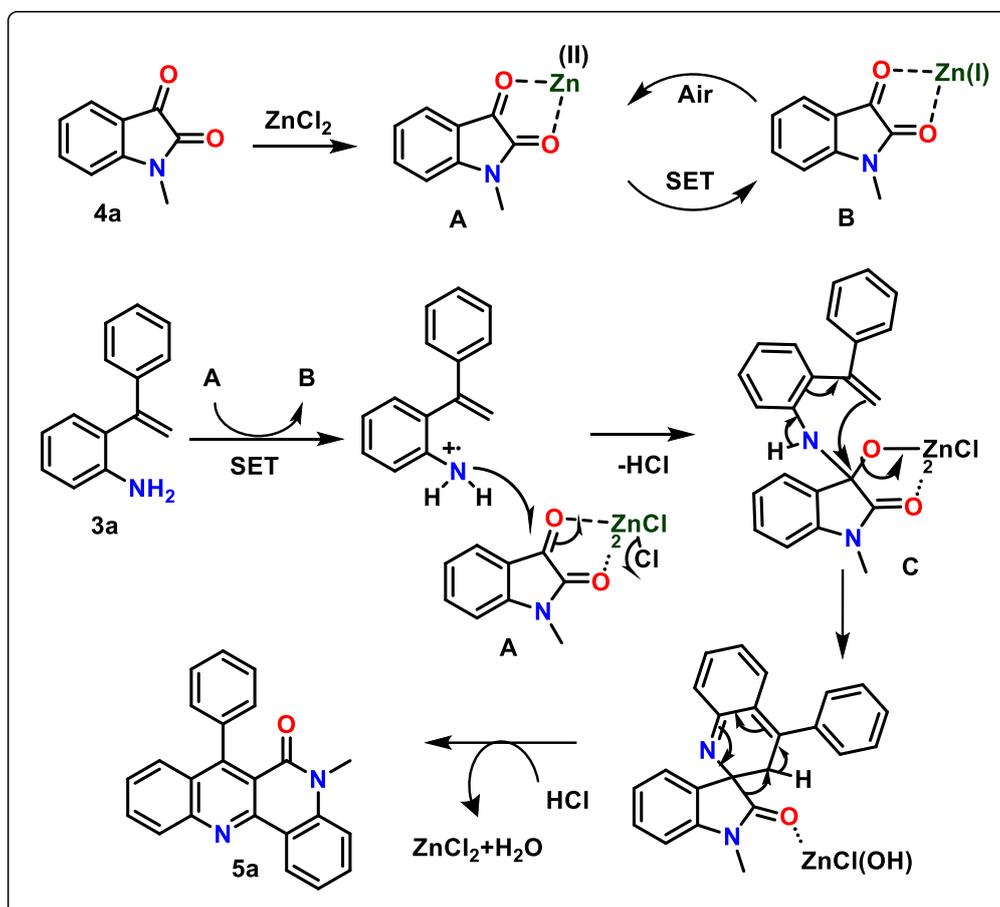
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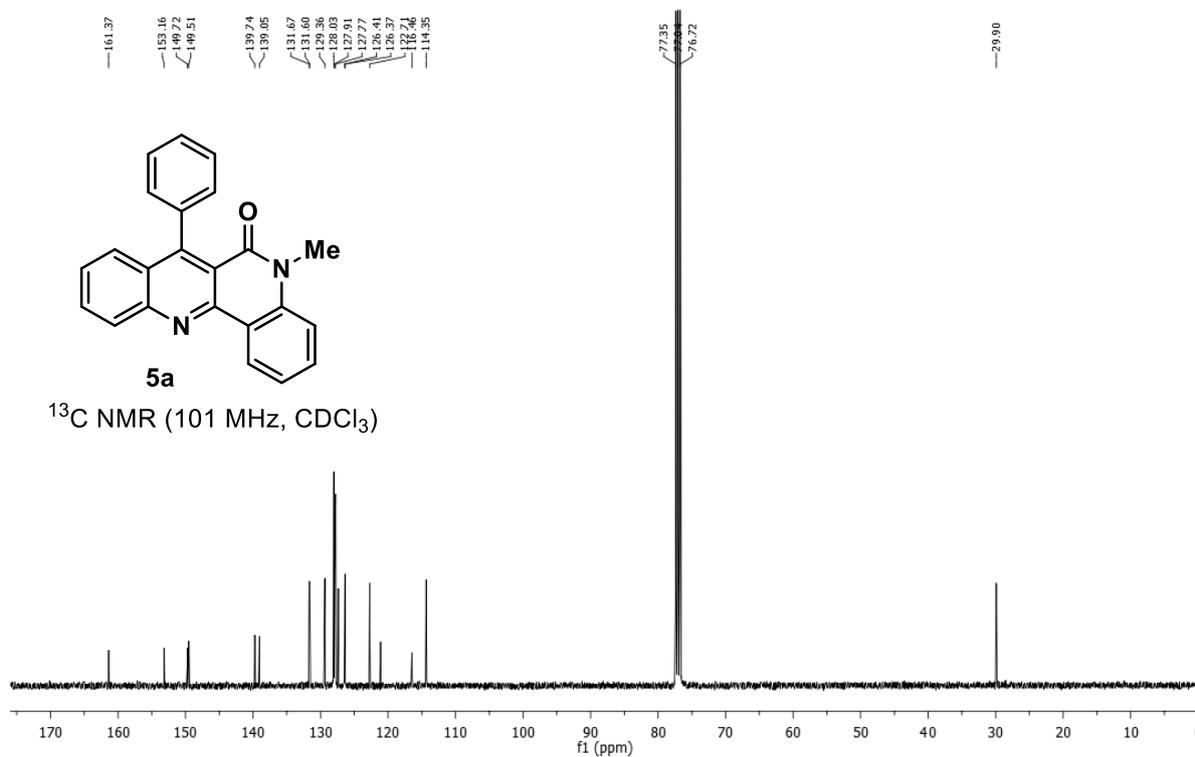
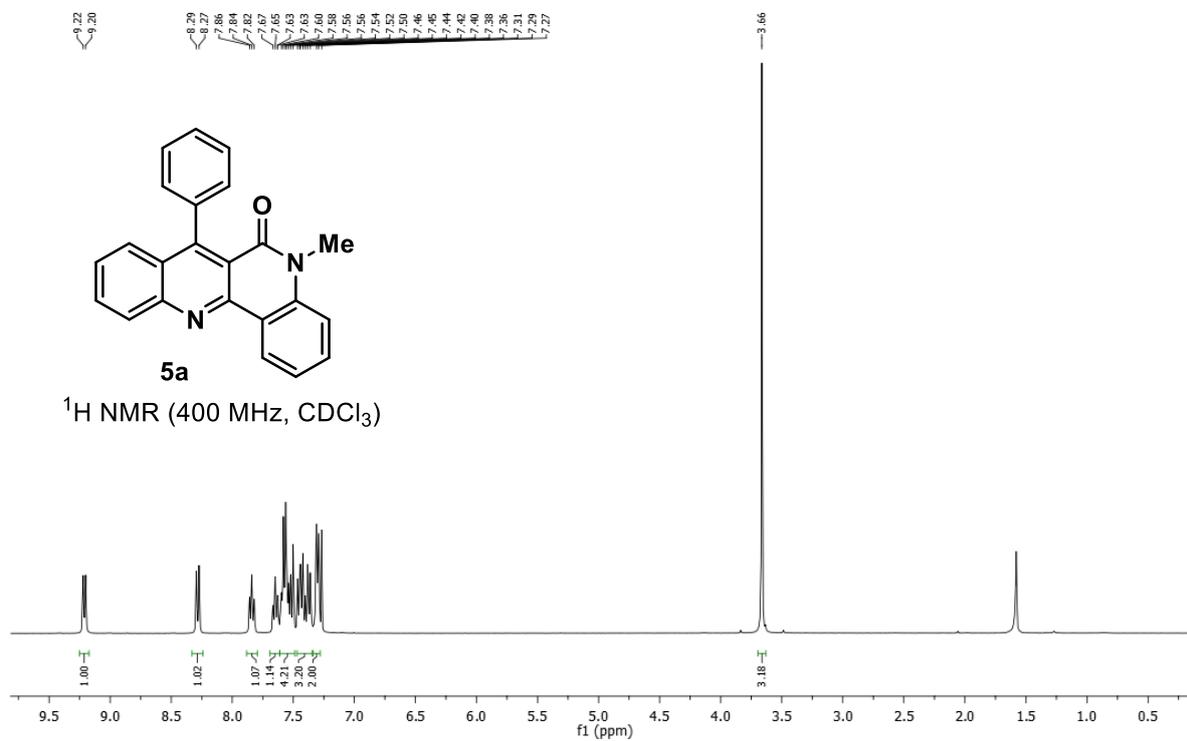
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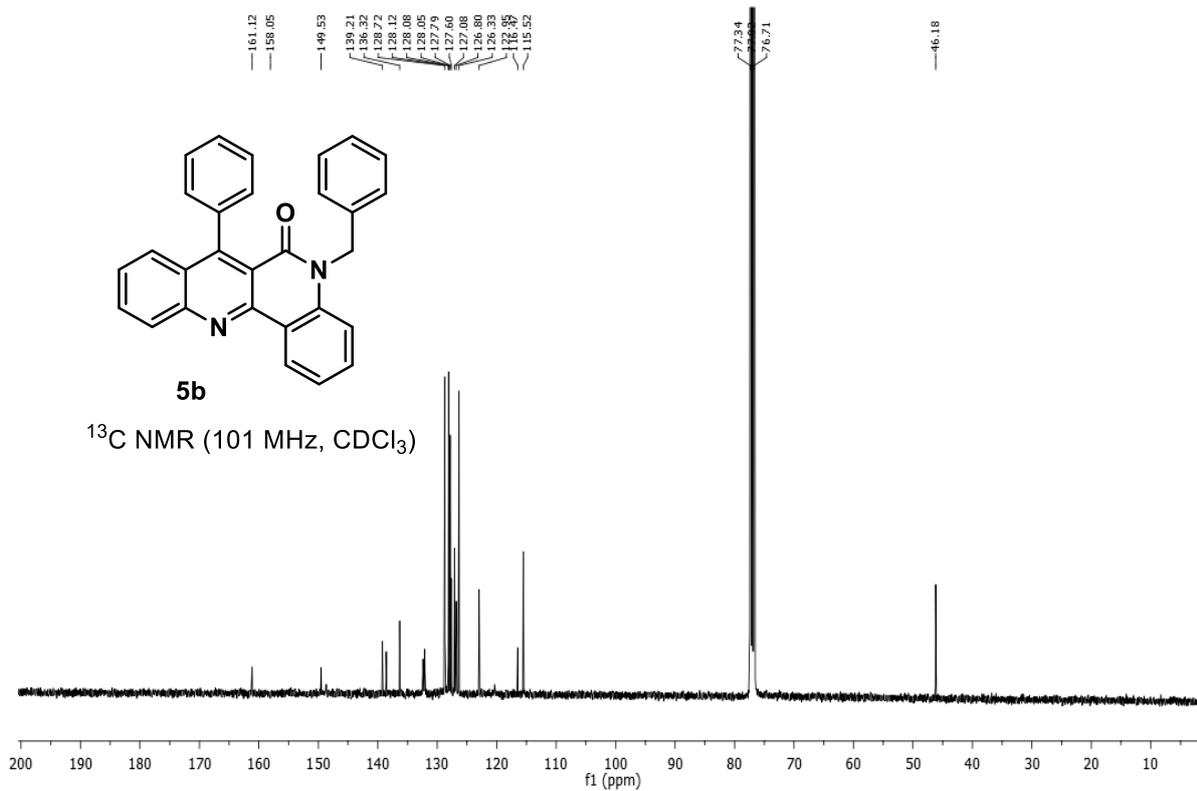
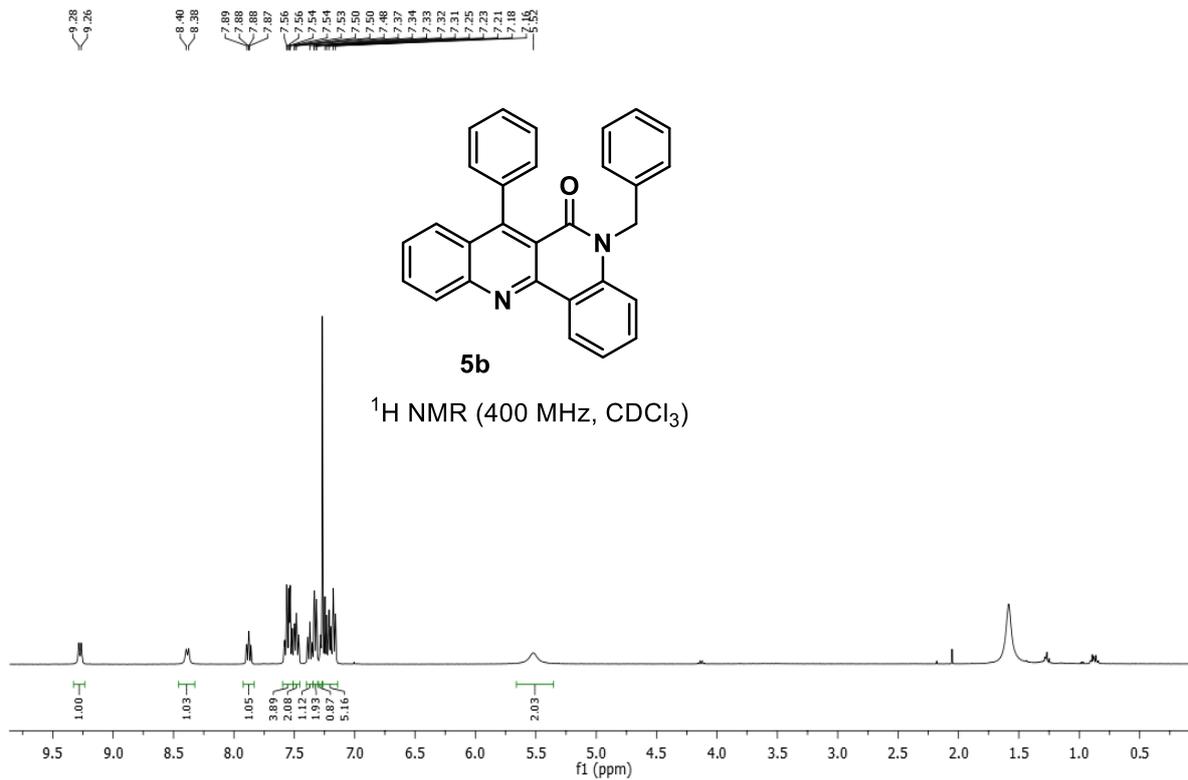
# 1. Reaction mechanism for the synthesis of quinoline-fused quinolone derivatives (5)

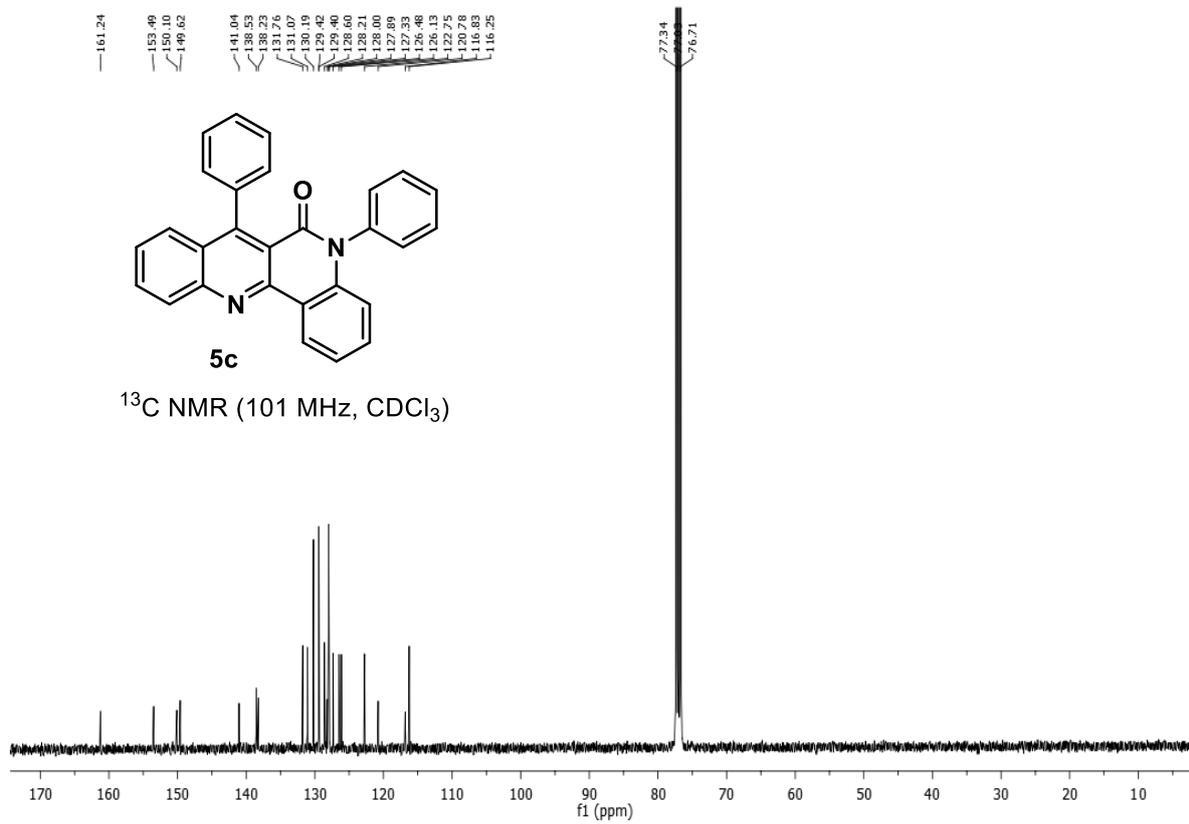
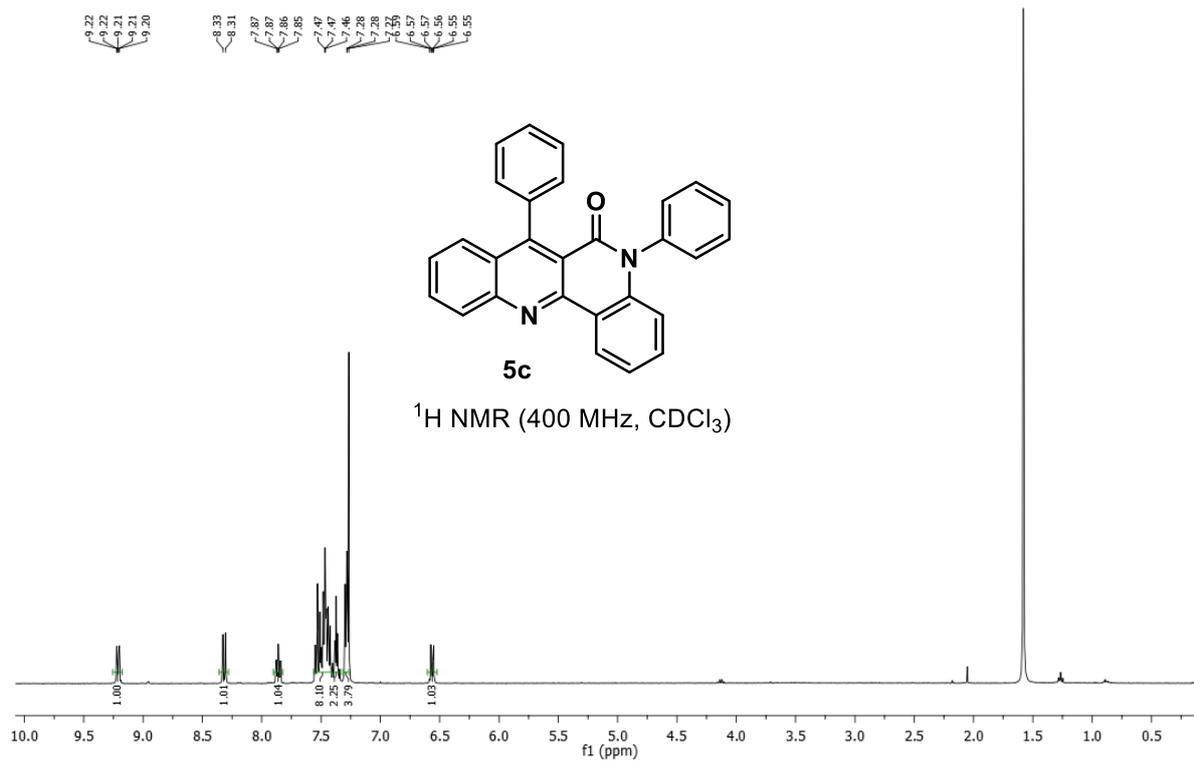


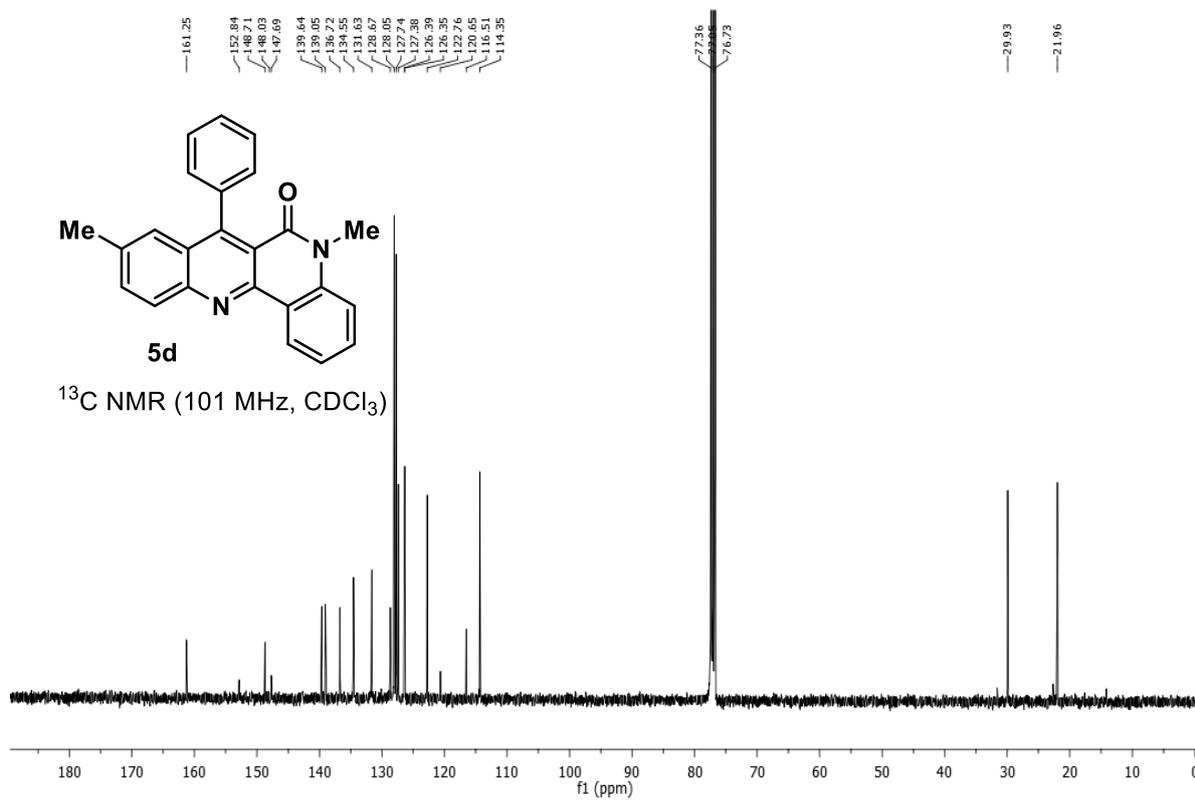
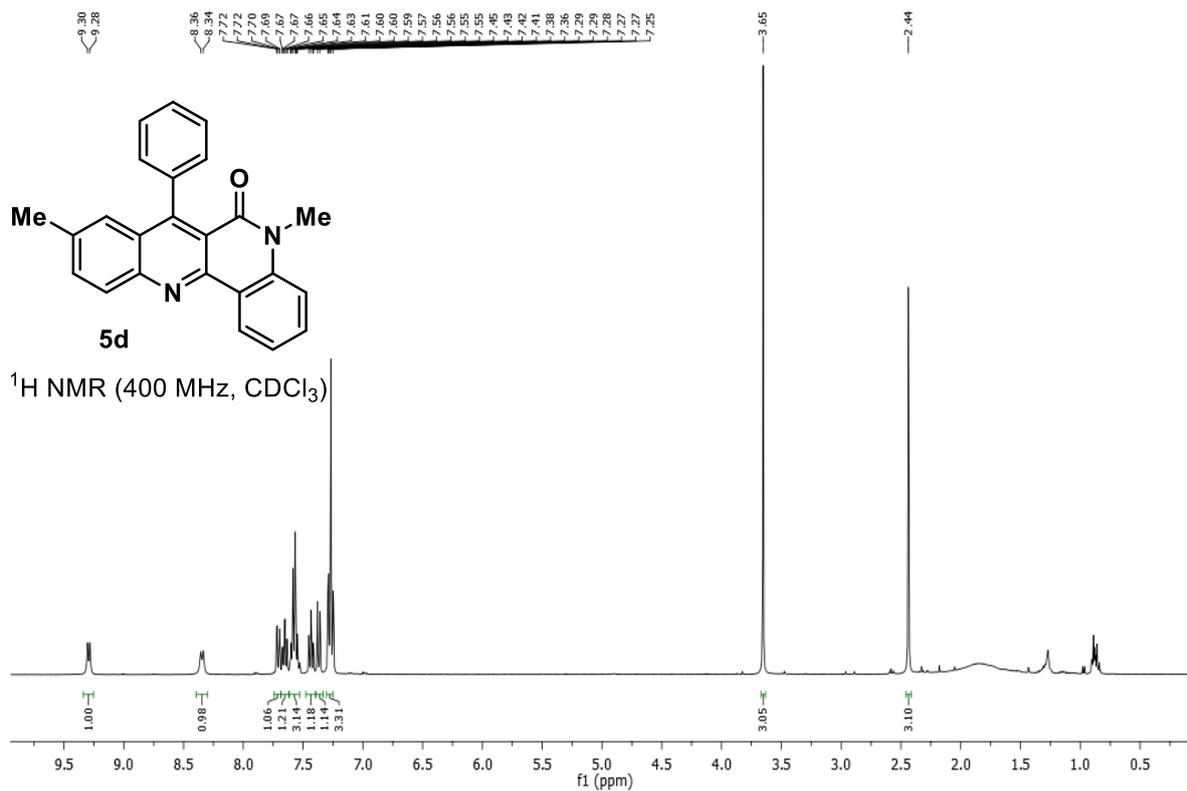
Scheme S1

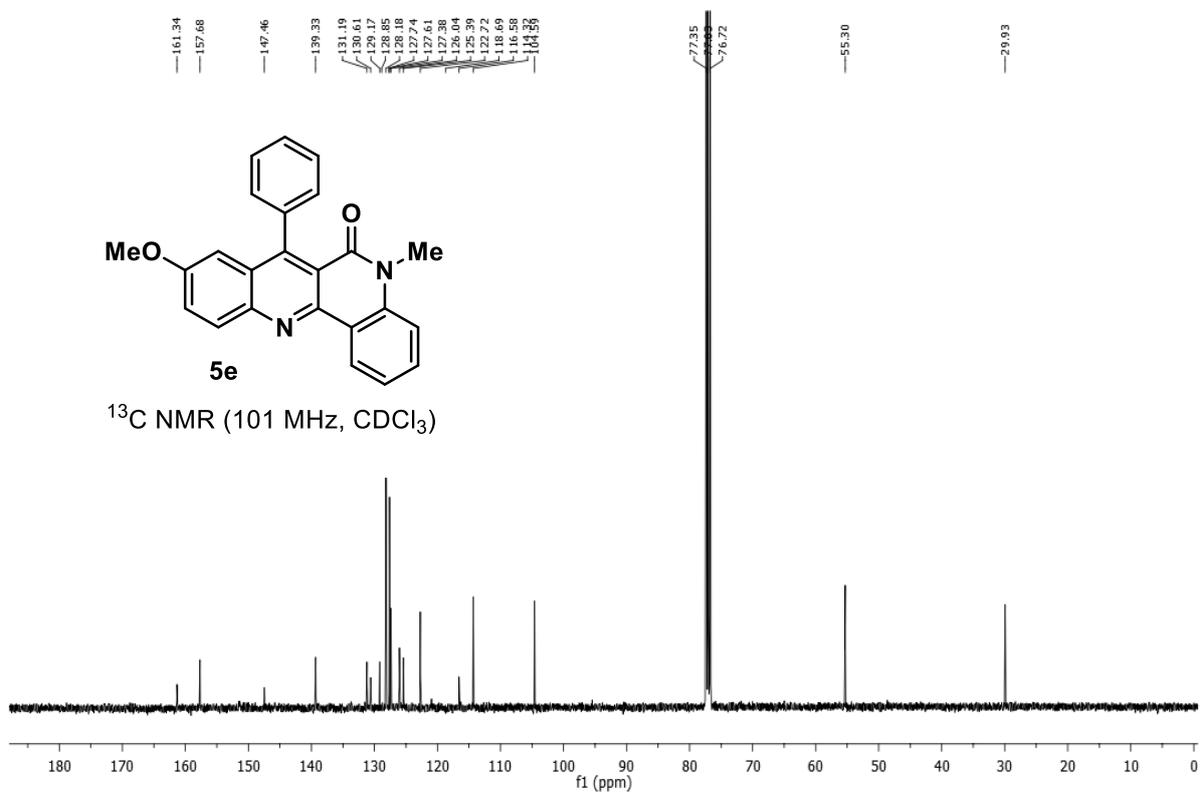
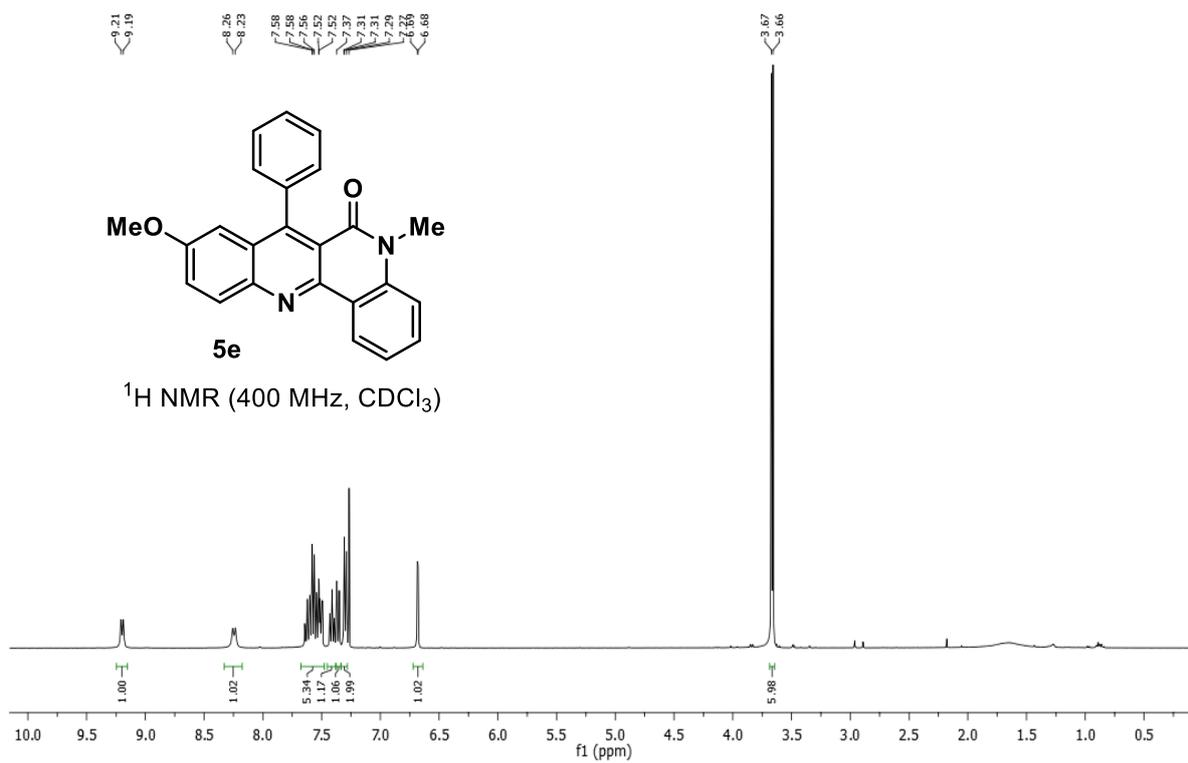
## 2. Copies of $^1\text{H}$ NMR & $^{13}\text{C}$ NMR Spectra of quinoline-fused quinolones

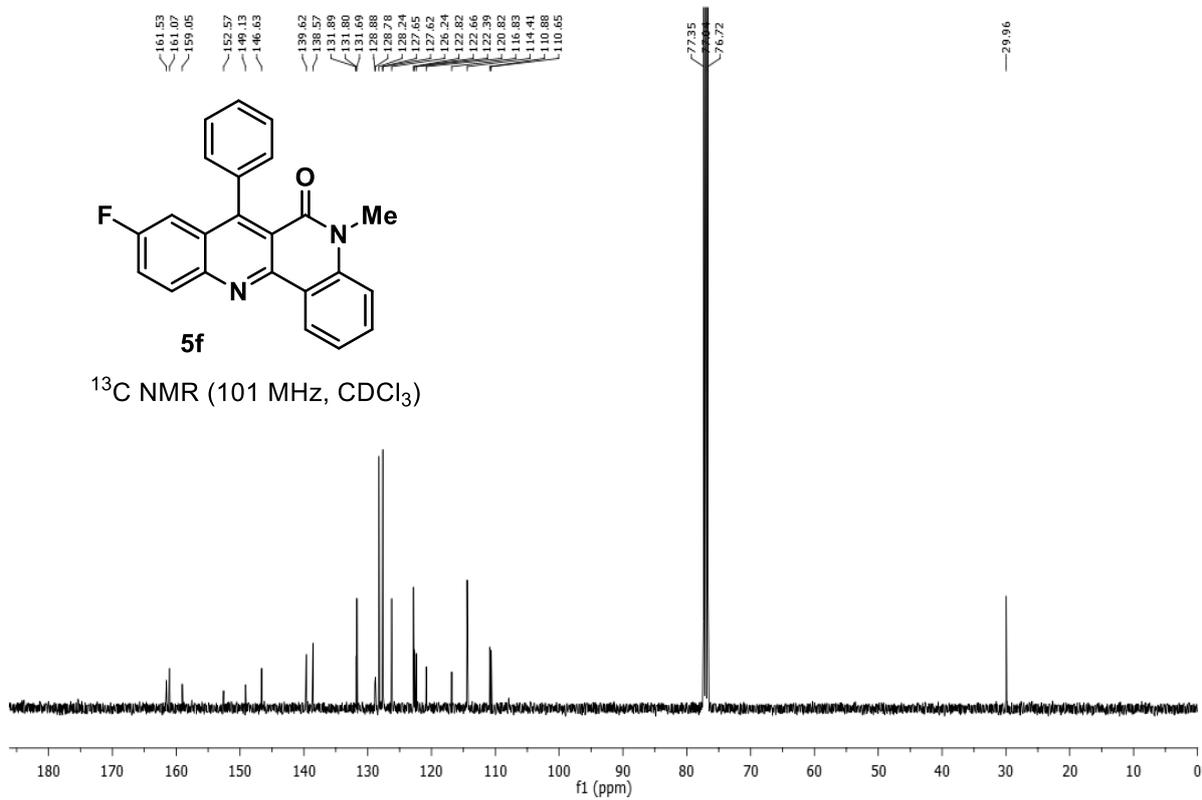
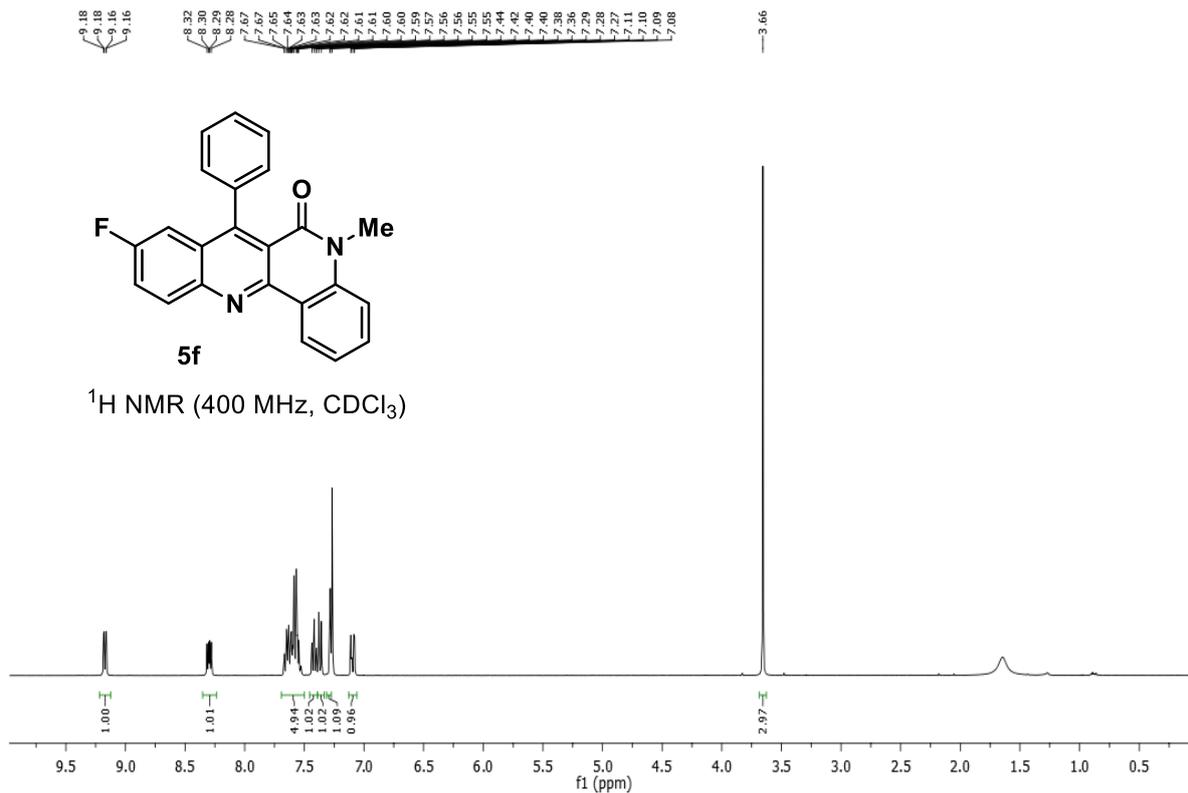


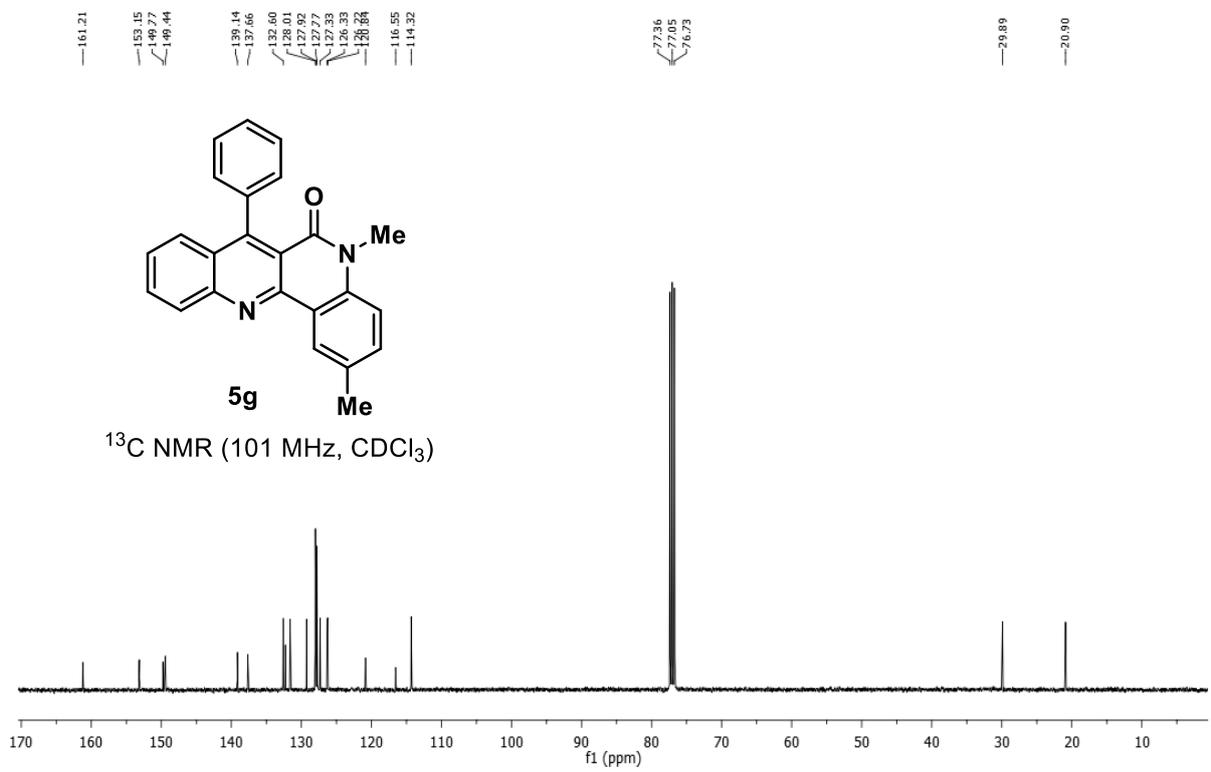
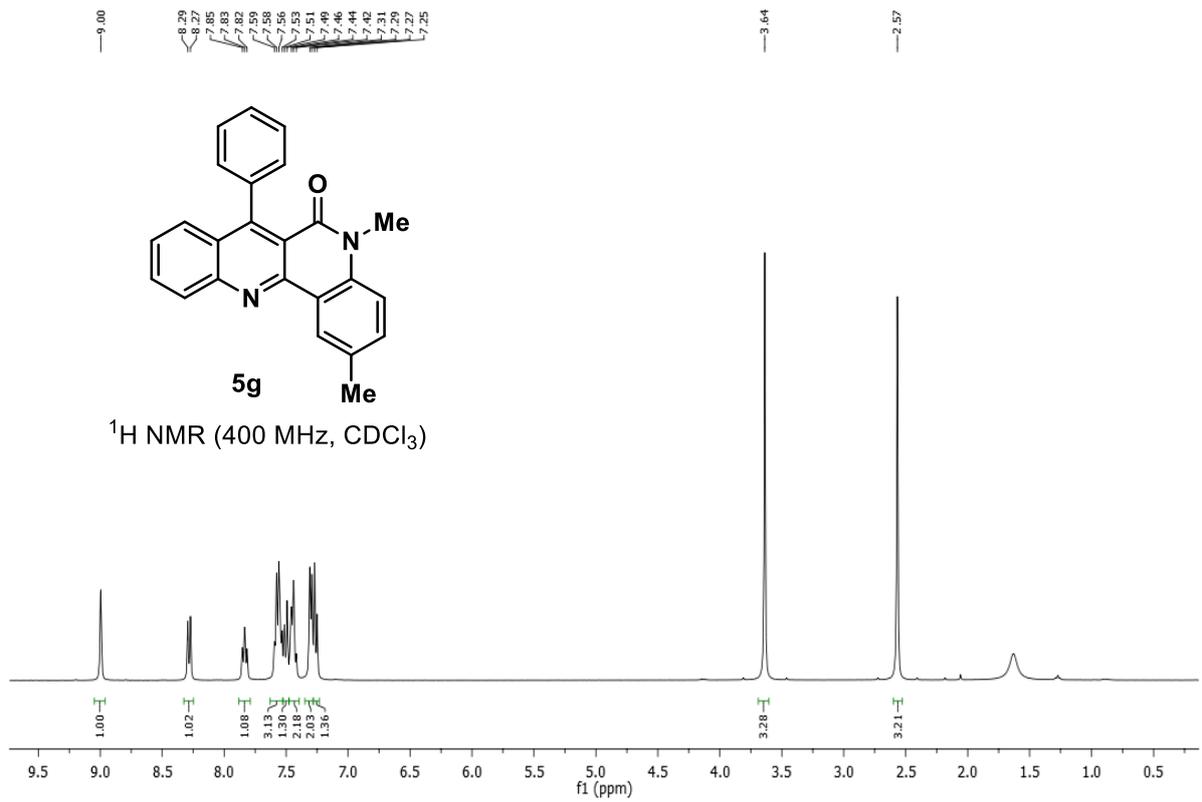


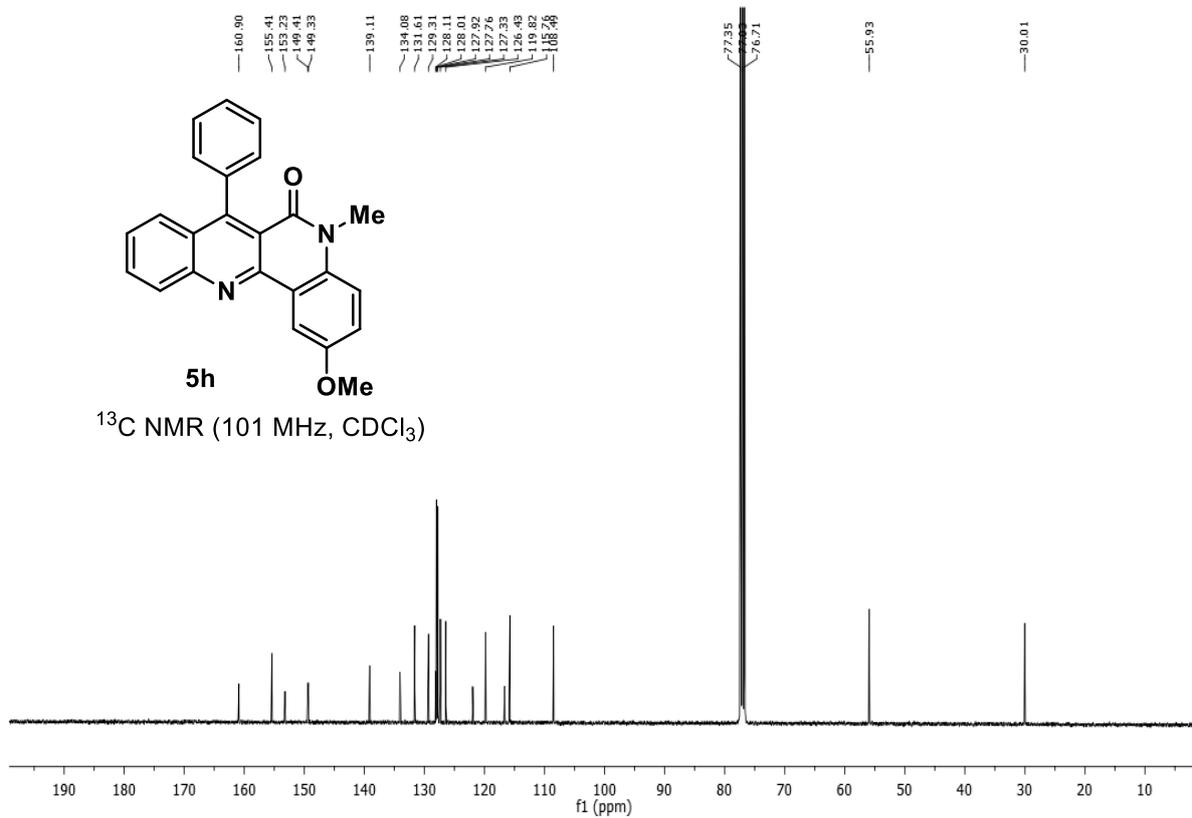
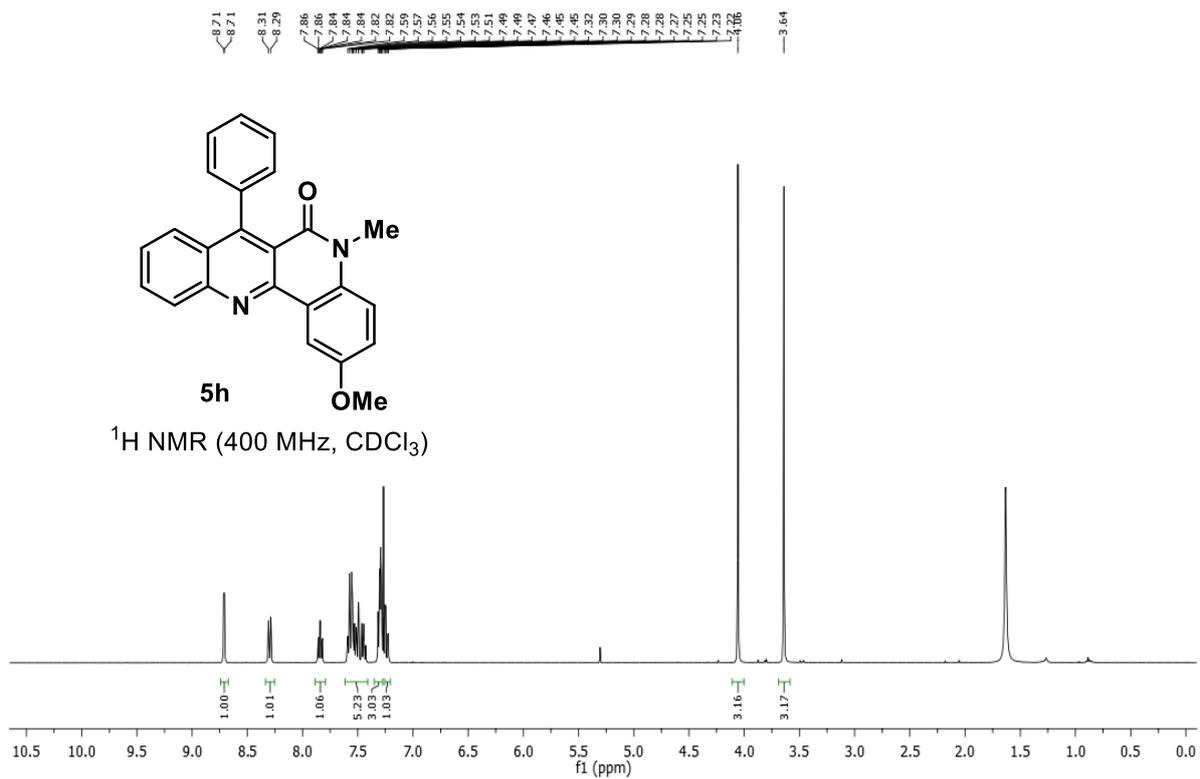


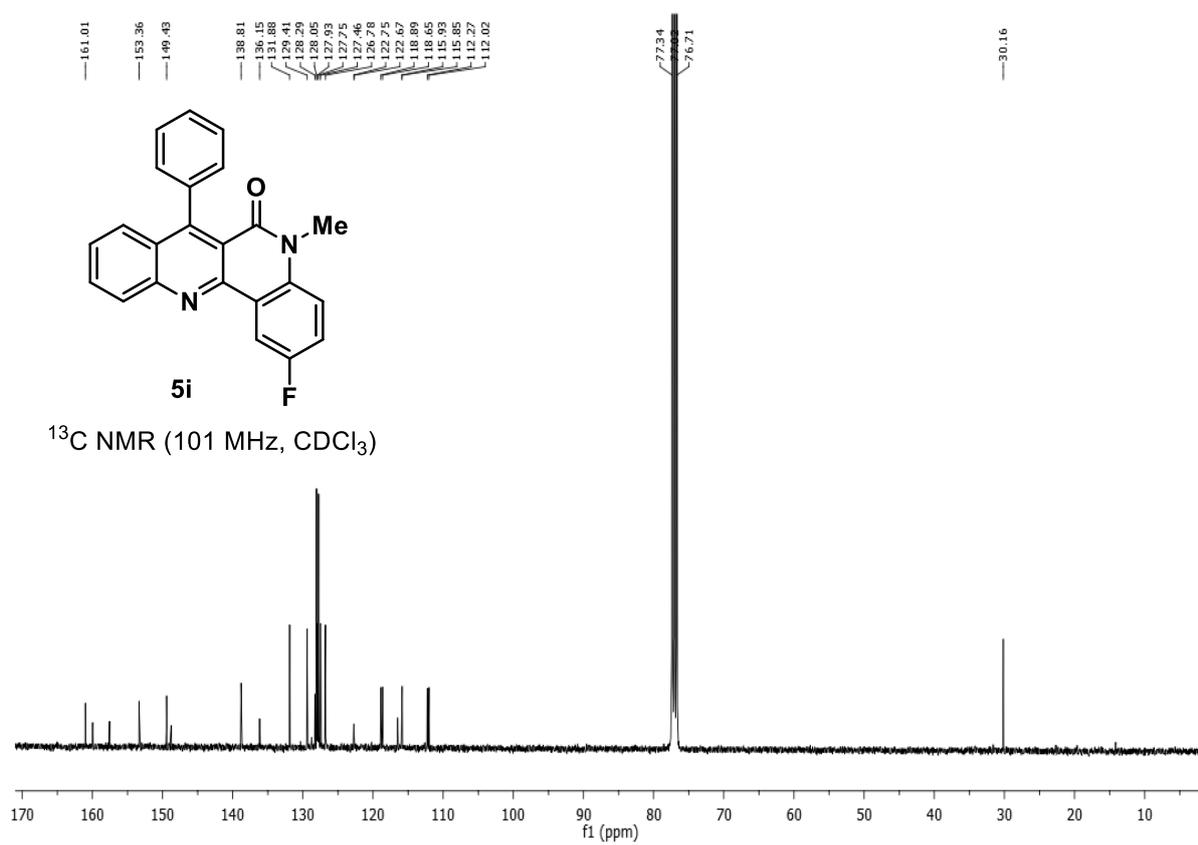
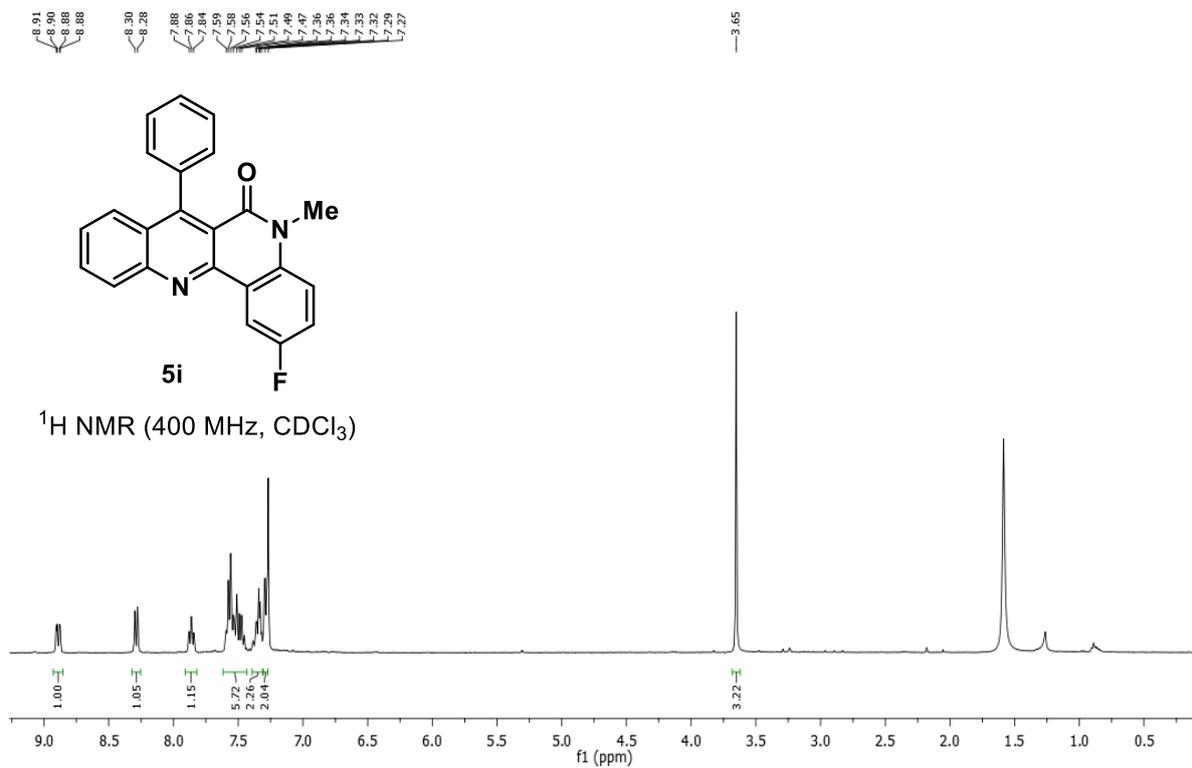


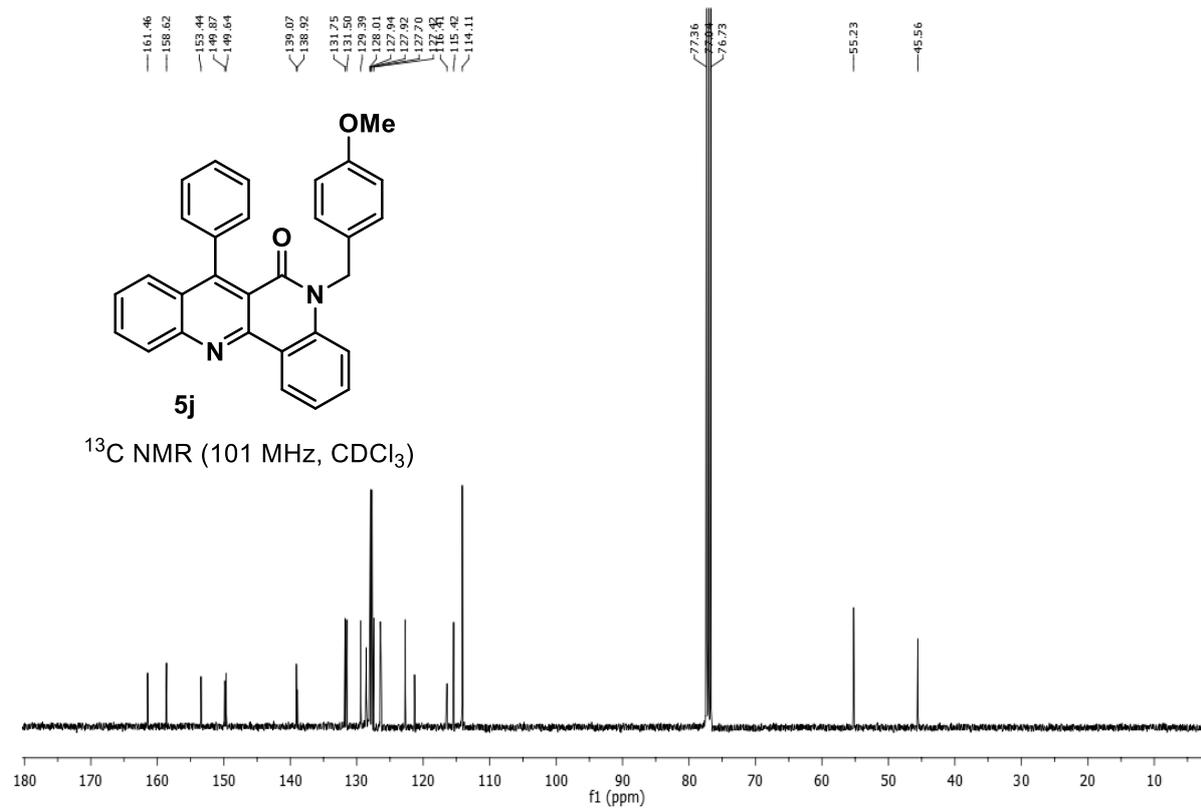
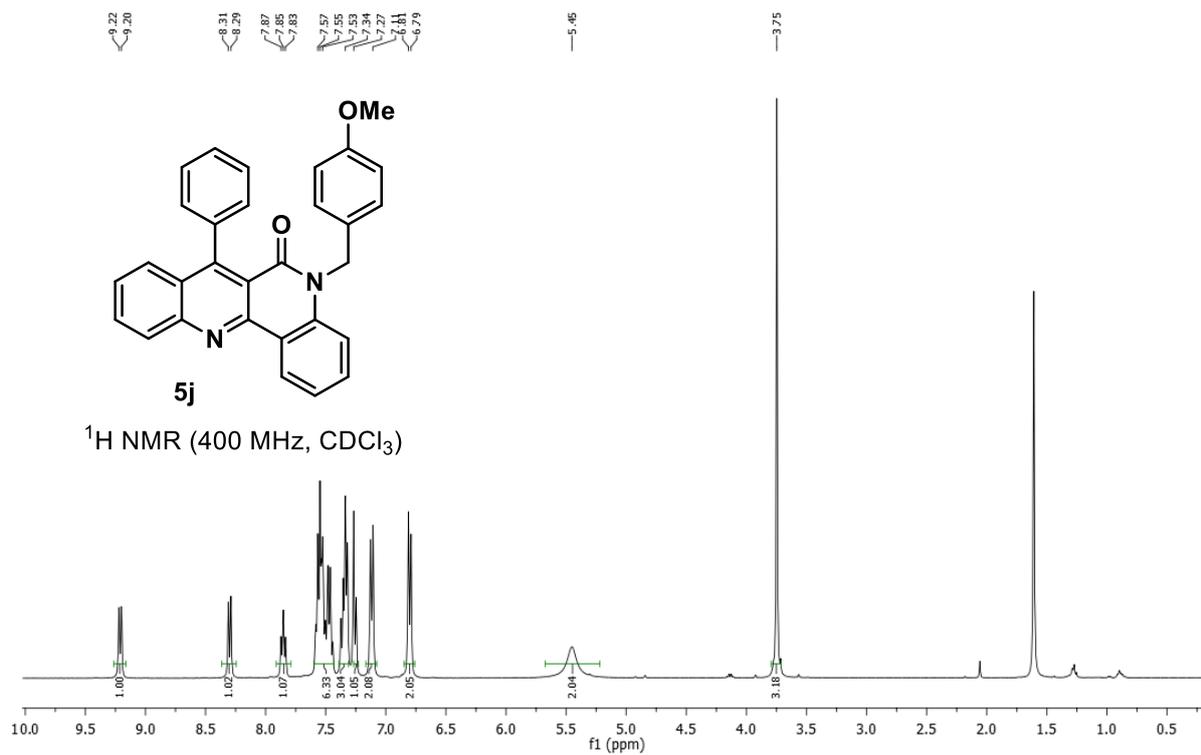


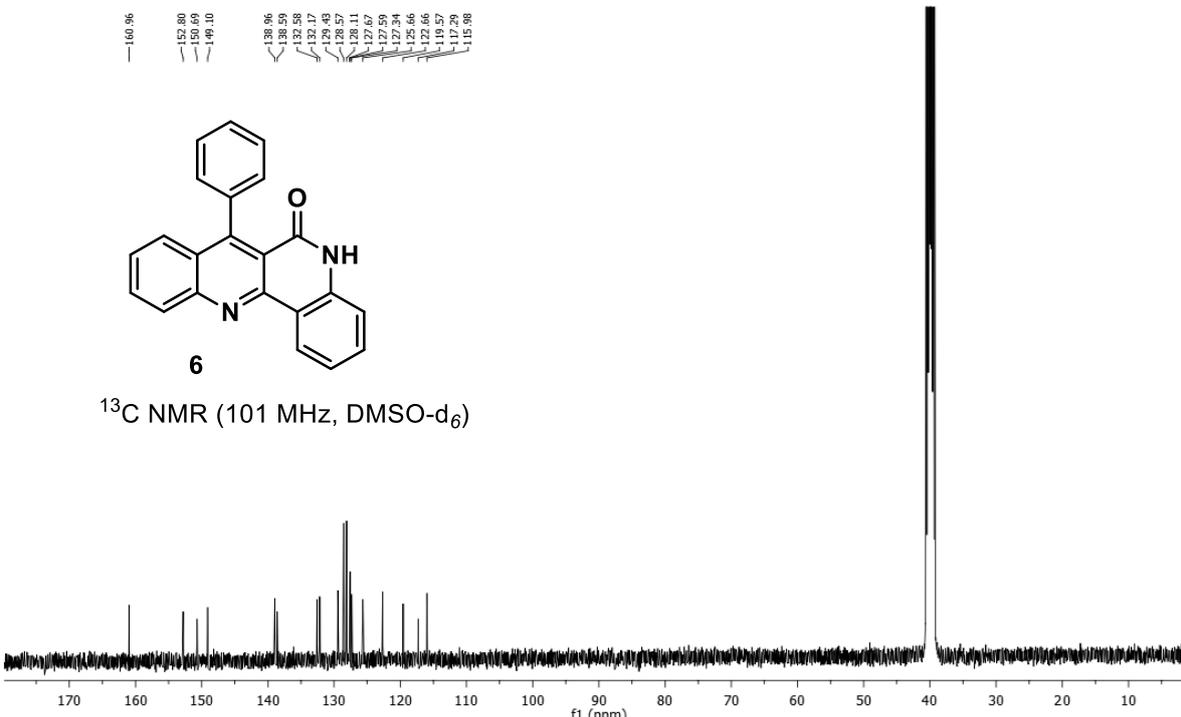
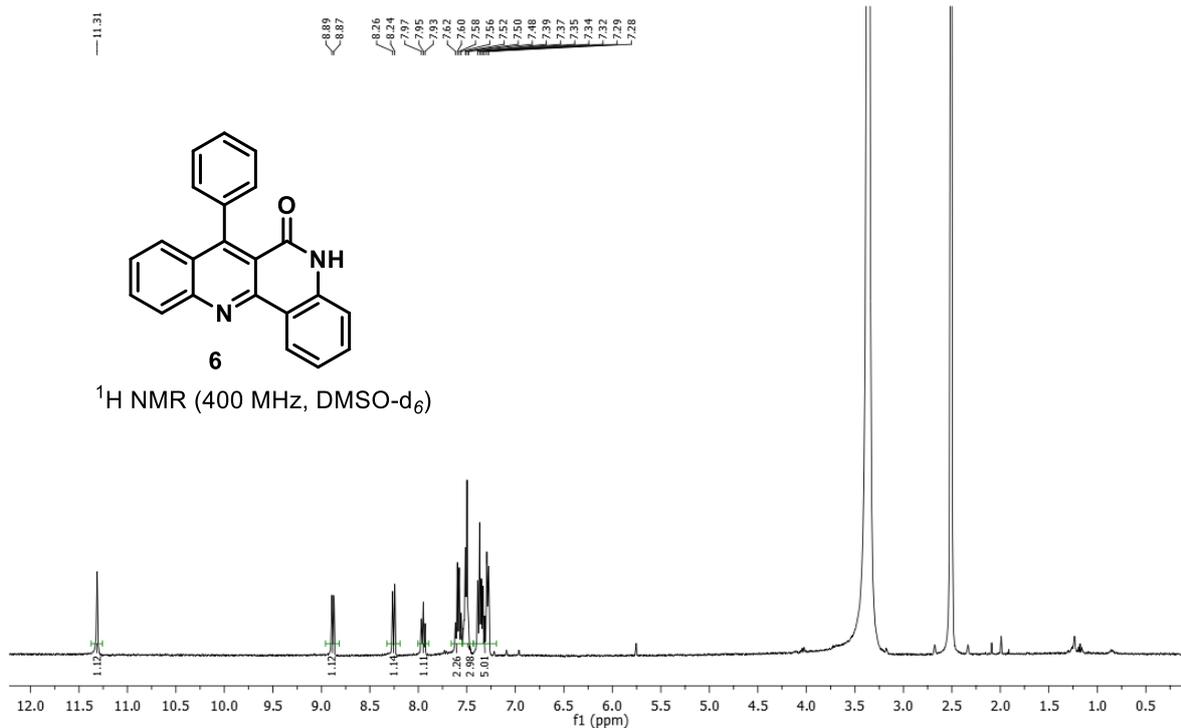




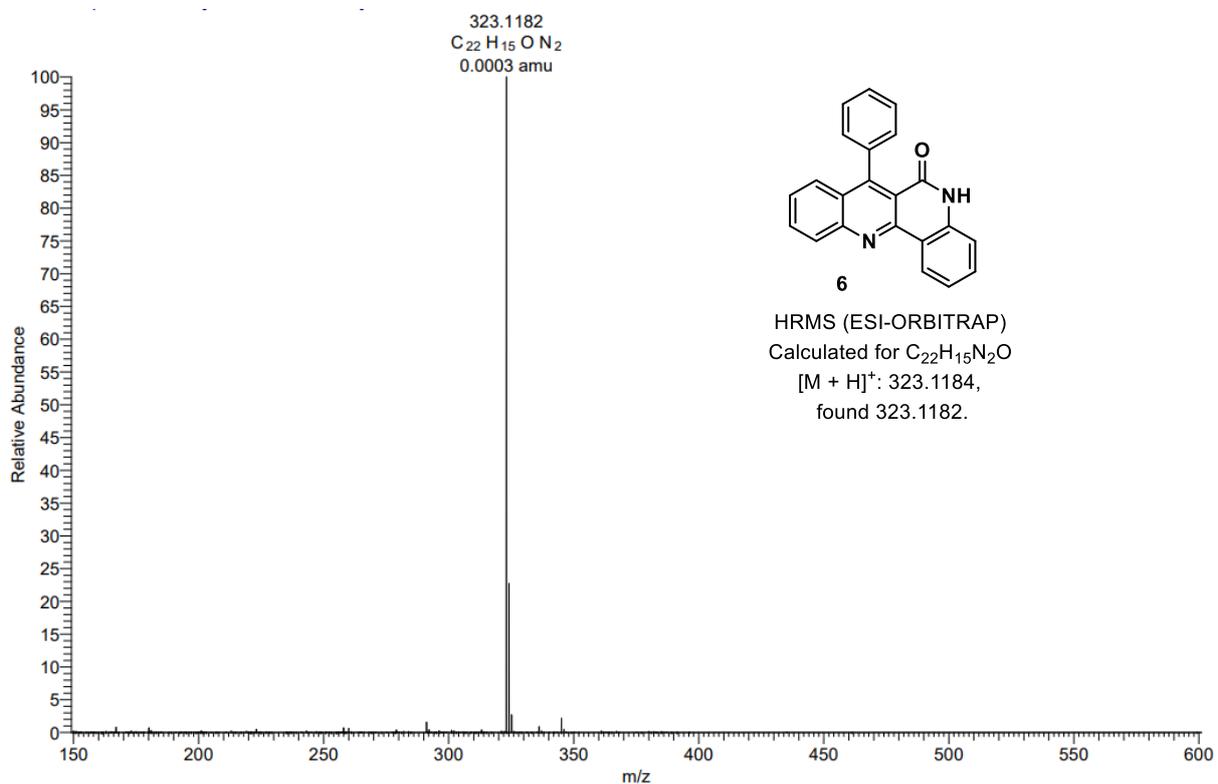
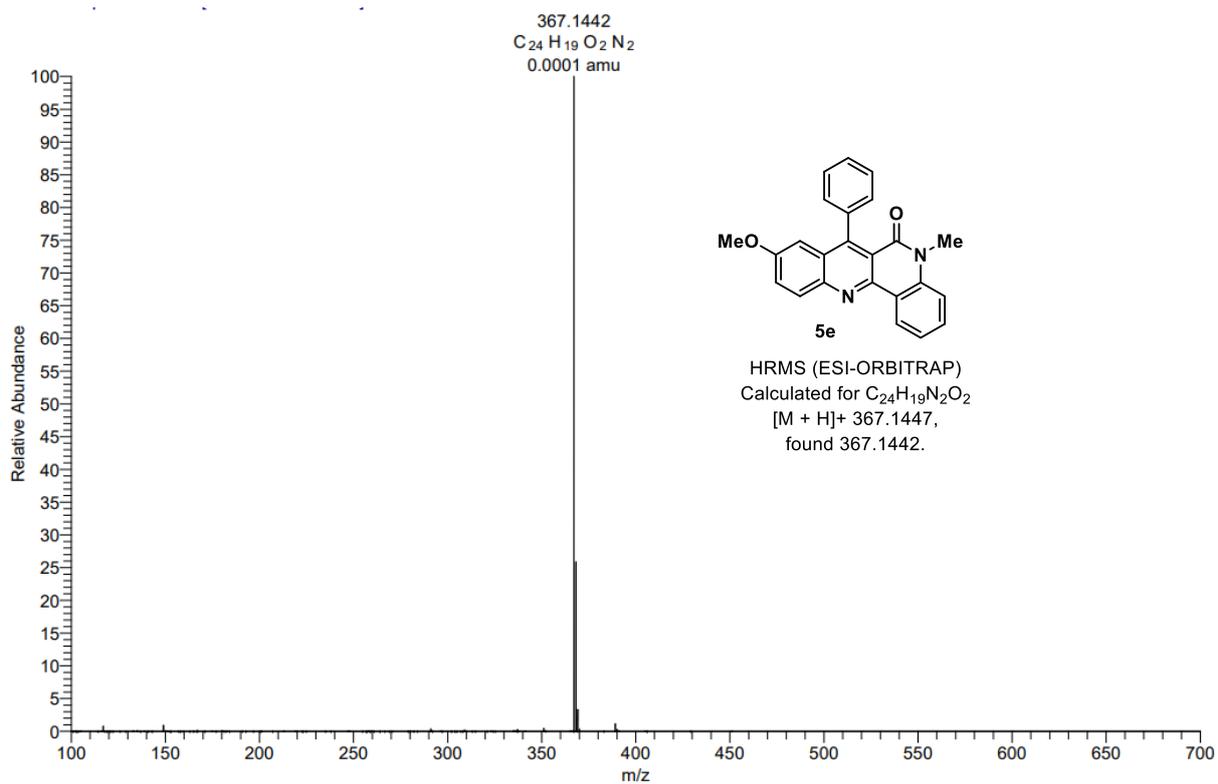




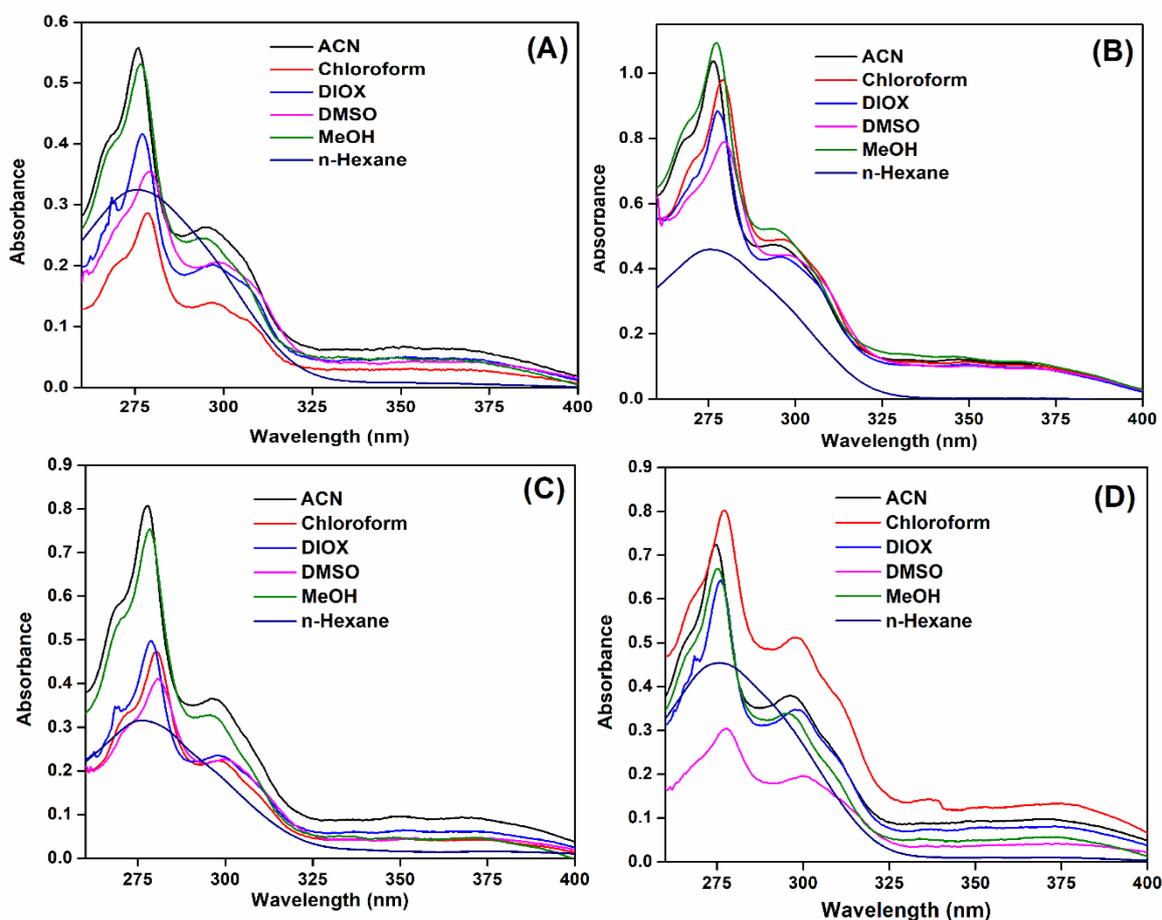




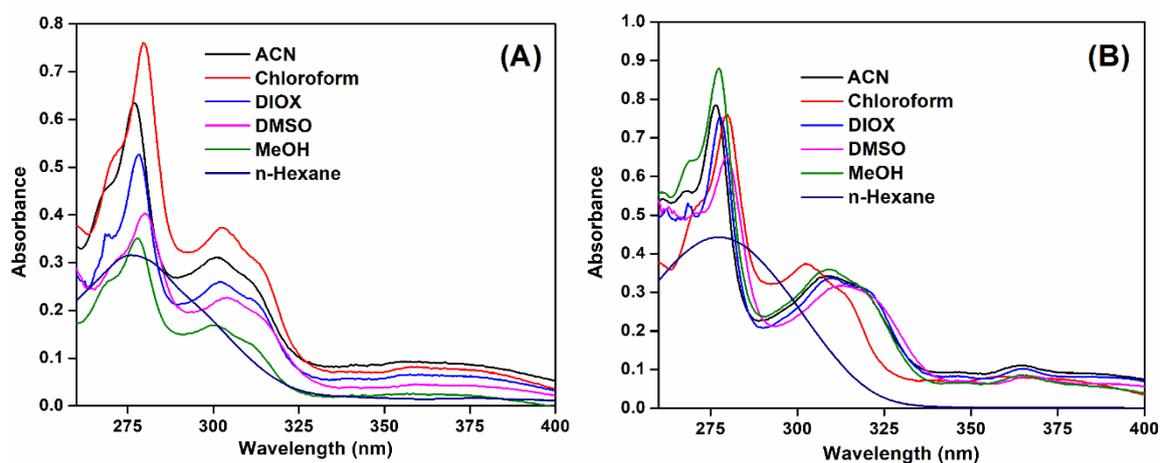
### 3. HRMS Spectra of compounds 5e and 6



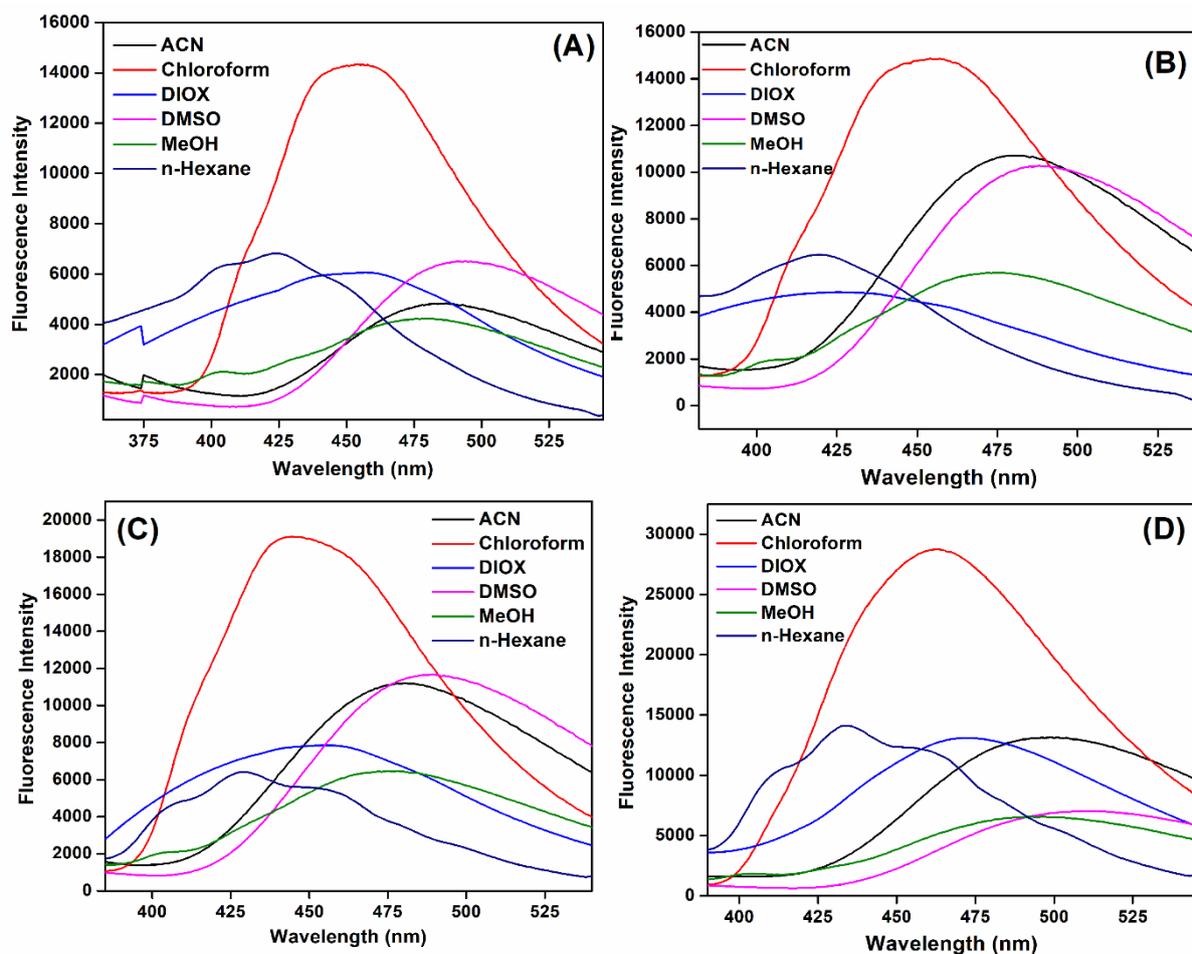
#### 4. Photophysical studies in different organic solvents (Solvatochromism)



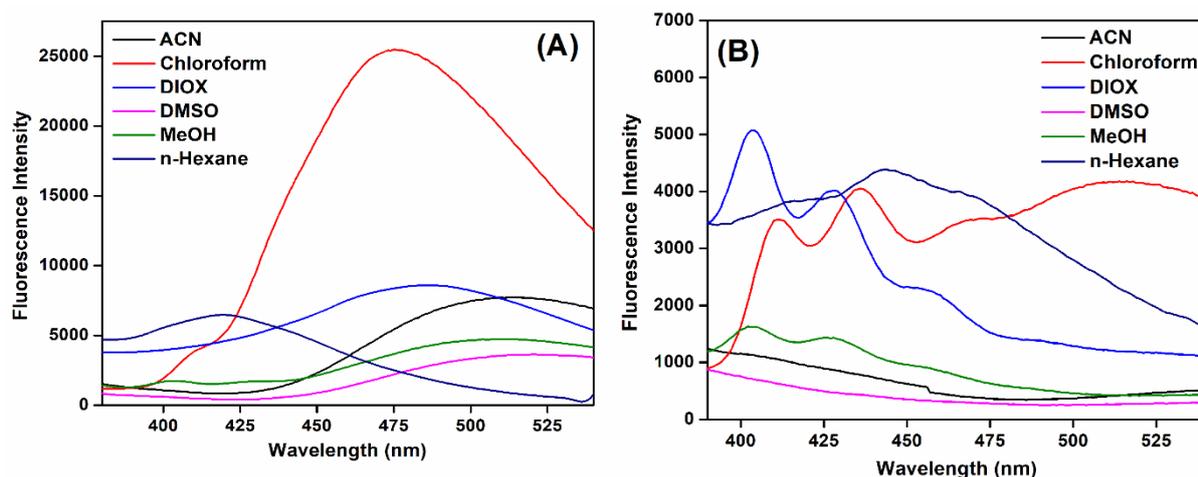
**Fig. S1** Absorption spectral curves of compounds **5a** (A), **5c** (B), **5d** (C) and **5f** (D) in solutions of six different solvents ( $1 \times 10^{-5}$  M).



**Fig. S2** Absorption spectral curves of compounds **5g** (A) and **5h** (B) in solutions of six different solvents ( $1 \times 10^{-5}$  M).



**Fig. S3** Emission spectral curves of compounds **5a** (A), **5c** (B), **5d** (C) and **5f** (D) in solutions of six different solvents ( $4 \times 10^{-6}$  M).



**Fig. S4** Emission spectral curves of compounds **5g** (A) and **5h** (B) in solutions of six different solvents ( $4 \times 10^{-6}$  M).

## 5. Calculation of quantum yield ( $\Phi_F$ ) in different solvents:

Fluorescence quantum yields ( $\Phi_F$ ) of all the synthesized molecules were measured considering quinine sulfate in 0.5 (M)  $H_2SO_4$  ( $\Phi_f^{ref} = 0.546$ ) as a reference fluorescent compound. Fluorescence quantum yields were calculated using the following equation (1)

$$\Phi_f = \frac{F_s A_{ref} \eta_s^2}{F_{ref} A_s \eta_{ref}^2} \Phi_f^{ref} \quad (1)$$

Where,  $F_s$  and  $F_{ref}$  are the areas of the fluorescence spectrum for sample and reference respectively.  $A_s$  and  $A_{ref}$  represent the absorbances at the excitation wavelength for sample and reference respectively.  $\eta_s$  and  $\eta_{ref}$  are the refractive indexes of sample solvent and reference compound solvent respectively.<sup>1</sup>

**Table S1** Absorbance ( $A_s$ ) and fluorescence emission area ( $F_s$ ) quinoline-fused quinolone derivatives (**5a-i** & **6**) in different solvents [Concentration of the Probe is  $4 \times 10^{-6}$  M].

Compound	Solvents	Absorbance ( $A_s$ )	Emission area ( $F_s$ )
<b>5a</b>	MeOH	0.098	247429.86
	Acetonitrile	0.124	291331.69
	Dimethyl sulfoxide	0.076	400835.22
	Chloroform	0.109	295958.34
	1,4 Dioxane	0.114	376846.87
	n-hexane	0.093	297369.33
<b>5b</b>	MeOH	0.062	458072.92
	Acetonitrile	0.194	922961.53
	Dimethyl sulfoxide	0.109	511026.95
	Chloroform	0.188	1317092.3
	1,4 Dioxane	0.090	420305.14
	n-hexane	0.160	368003.91
<b>5c</b>	MeOH	0.091	421217.31
	Acetonitrile	0.083	790315.15
	Dimethyl sulfoxide	0.127	758061.82
	Chloroform	0.151	1224663.3
	1,4 Dioxane	0.046	153139.33
	n-hexane	0.128	322201.14
<b>5d</b>	MeOH	0.062	478190.95
	Acetonitrile	0.134	838338.46
	Dimethyl sulfoxide	0.062	868124.86
	Chloroform	0.151	1596414.8
	1,4 Dioxane	0.042	560775.05
	n-hexane	0.110	327383.29
<b>5e</b>	MeOH	0.087	2016866.73
	Acetonitrile	0.057	692207.30
	Dimethyl sulfoxide	0.055	592344.86
	Chloroform	0.095	4683802.9
	1,4 Dioxane	0.152	1524094.44

	n-hexane	0.092	1668460.18
<b>5f</b>	MeOH	0.046	427394.52
	Acetonitrile	0.103	857499.84
	Dimethyl sulfoxide	0.050	409558.52
	Chloroform	0.075	2439614.4
	1,4 Dioxane	0.095	879104.08
	n-hexane	0.073	748778.21
<b>5g</b>	MeOH	0.111	221264.56
	Acetonitrile	0.114	426582.96
	Dimethyl sulfoxide	0.112	178114.05
	Chloroform	0.102	2057562.8
	1,4 Dioxane	0.290	518102.58
	n-hexane	0.095	294537.80
<b>5h</b>	MeOH	0.041	22854.0
	Acetonitrile	0.138	55237.1
	Dimethyl sulfoxide	0.144	38413.0
	Chloroform	0.084	342410.2
	1,4 Dioxane	0.118	62477.0
	n-hexane	0.078	112237.23
<b>5i</b>	MeOH	0.052	257470.91
	Acetonitrile	0.039	471371.38
	Dimethyl sulfoxide	0.052	402139.55
	Chloroform	0.064	1129541.1
	1,4 Dioxane	0.035	331838.04
	n-hexane	0.063	222052.68
<b>6</b>	MeOH	0.111	1411627.01
	Acetonitrile	0.143	1390510.31
	Dimethyl sulfoxide	0.192	2322840.88
	Chloroform	0.158	1065314.67
	1,4 Dioxane	0.165	973999.15
	n-hexane	0.149	391111.76

( $A_{ref}$ ) of the Quinine sulfate ( $4 \times 10^{-6}$  M) in 0.5 (M)  $H_2SO_4 = 0.060$ ; ( $F_{ref}$ ) of the Quinine sulfate ( $4 \times 10^{-6}$  M) in 0.5 (M)  $H_2SO_4 = 2416797.6$ ; Refractive index of 0.5 (M)  $H_2SO_4$  ( $\eta_{ref}$ ) = 1.418. Refractive indexes of different solvents:  $\eta_{ACN} = 1.34$ ,  $\eta_{MeOH} = 1.328$ ,  $\eta_{DMSO} = 1.479$ ,  $\eta_{CHCl_3} = 1.446$ ,  $\eta_{DIOX} = 1.421$ .  $\eta_{n-hexane} = 1.375$ .

## 6. Compound 6 in different pH

A set of buffer solutions covering the pH range 1-8 was prepared. An HCl/KCl buffer was prepared for pH 1, a glycine/HCl buffer for pH 2-3, an acetate buffer (acetic acid/sodium acetate) for pH 4-6, a (PBS) phosphate buffer (dihydrogen phosphate/hydrogen phosphate) for pH 7-7.2, and a 1.5 M Tris-HCl buffer for pH 8. Spectrofluorometric titration of **6** ( $4 \times 10^{-6}$  M) was performed using the different buffer solutions in a DMSO-water (8:2, v/v) solvent system.

## 7. Calculation of limit of detection (LOD)

Limit of detection (LOD) of fluorescent sensor was calculated using the equation ( $3 \times \sigma / K$ ), where  $\sigma$  represents the standard deviation (S.D.) of the intensity of free fluorescent probe that was measured by recording 10 times emission intensity of the blank probe and  $K$  is the slope of the linear plot of fluorescence intensity vs. concentration of analyte.

From Graph, we get  $\sigma = 9.31904$

### i) LOD for $\text{Cu}^{2+}$ :

$$\text{Slop } K = 5.3226 \times 10^8$$

$$\text{Limit of detection (LOD) of compound } \mathbf{6} \text{ for } \text{Cu}^{2+} = 3 \times 9.31904 / (5.3226 \times 10^8) = 5.252 \times 10^{-8} \text{ M} = 52.52 \times 10^{-9} \text{ M} = 52.5 \text{ nM.}$$

### ii) LOD for $\text{Fe}^{3+}$ :

$$\text{Slop } K = 8.0143 \times 10^8$$

$$\text{LOD of compound } \mathbf{6} \text{ for } \text{Fe}^{3+}: 3 \times 9.31904 / (8.0143 \times 10^8) = 34.88 \times 10^{-9} \text{ M} = 34.88 \text{ nM.}$$

### iii) LOD for $\text{Hg}^{2+}$ :

$$\text{Slop } K = 1.69174 \times 10^9$$

$$\text{LOD of compound } \mathbf{6} \text{ for } \text{Hg}^{2+}: 3 \times 9.31904 / (1.69174 \times 10^9) = 16.52 \times 10^{-9} \text{ M} = 16.5 \text{ nM}$$

## 8. Calculation of limit of quantification (LOQ)

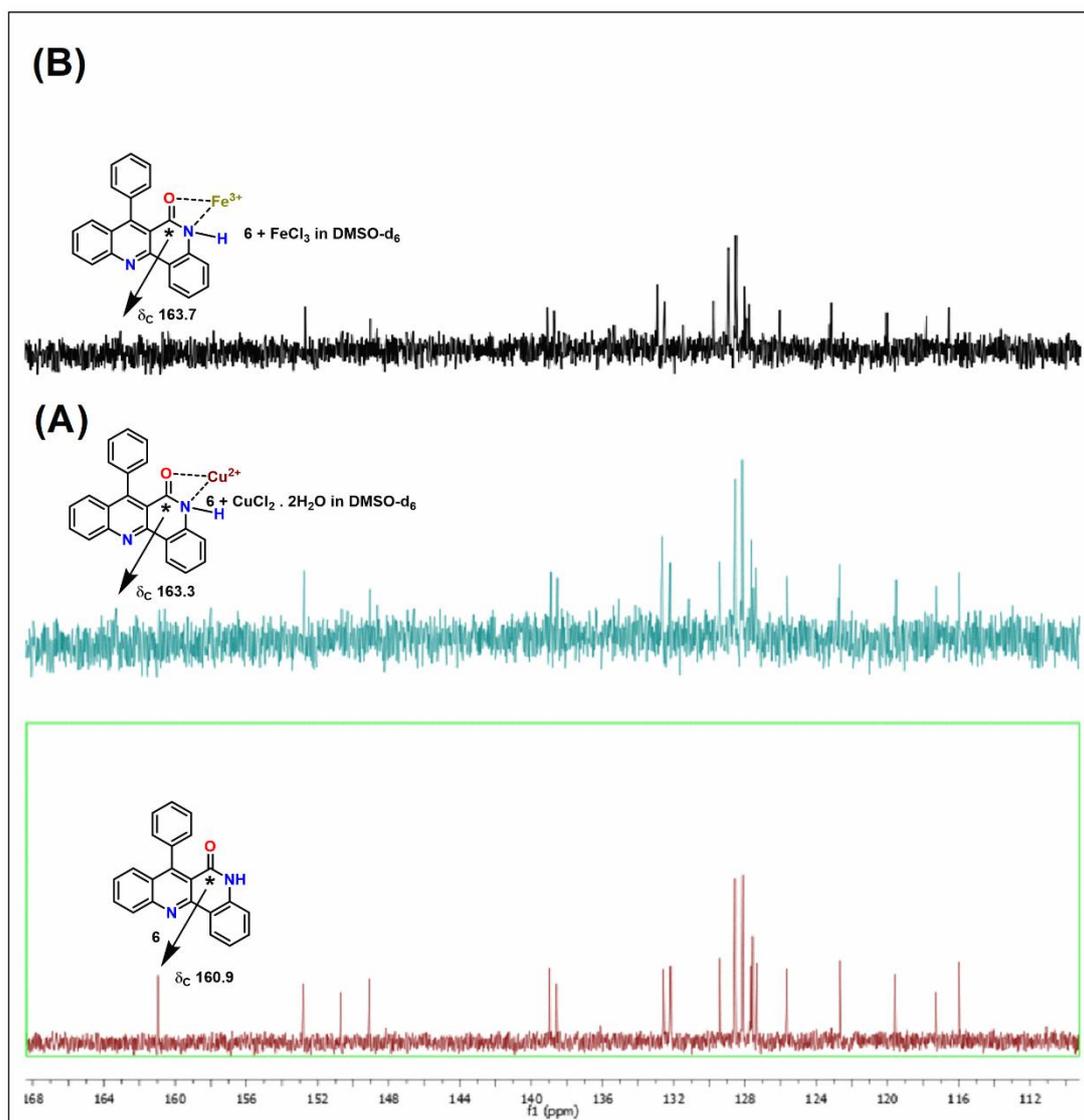
Limit of quantification (LOQ) of fluorescent sensor was calculated using the equation ( $10 \times \sigma / K$ ), where  $\sigma$  represents the standard deviation (S.D.) of the intensity of free fluorescent probe that was measured by recording 10 times emission intensity of the blank probe and  $K$  is the slope of the linear plot of fluorescence intensity vs. concentration of analyte.

$$\text{i) LOQ for } \text{Cu}^{2+}: 10 \times 9.31904 / (5.3226 \times 10^8) = 17.50 \times 10^{-8} \text{ M}$$

$$\text{ii) LOQ for } \text{Fe}^{3+}: 10 \times 9.31904 / (8.0143 \times 10^8) = 11.63 \times 10^{-8} \text{ M}$$

$$\text{iii) LOQ for } \text{Hg}^{2+}: 10 \times 9.31904 / (1.69174 \times 10^9) = 5.51 \times 10^{-8} \text{ M}$$

## 9. $^{13}\text{C}$ NMR Titration Experiments:



**Fig. S5**  $^{13}\text{C}$  NMR spectra of probe **6** in (A) presence of  $\text{Cu}^{2+}$  and (B) in presence of  $\text{Fe}^{3+}$  ions.

## 10. HRMS analysis of possible probe-metal complexes:

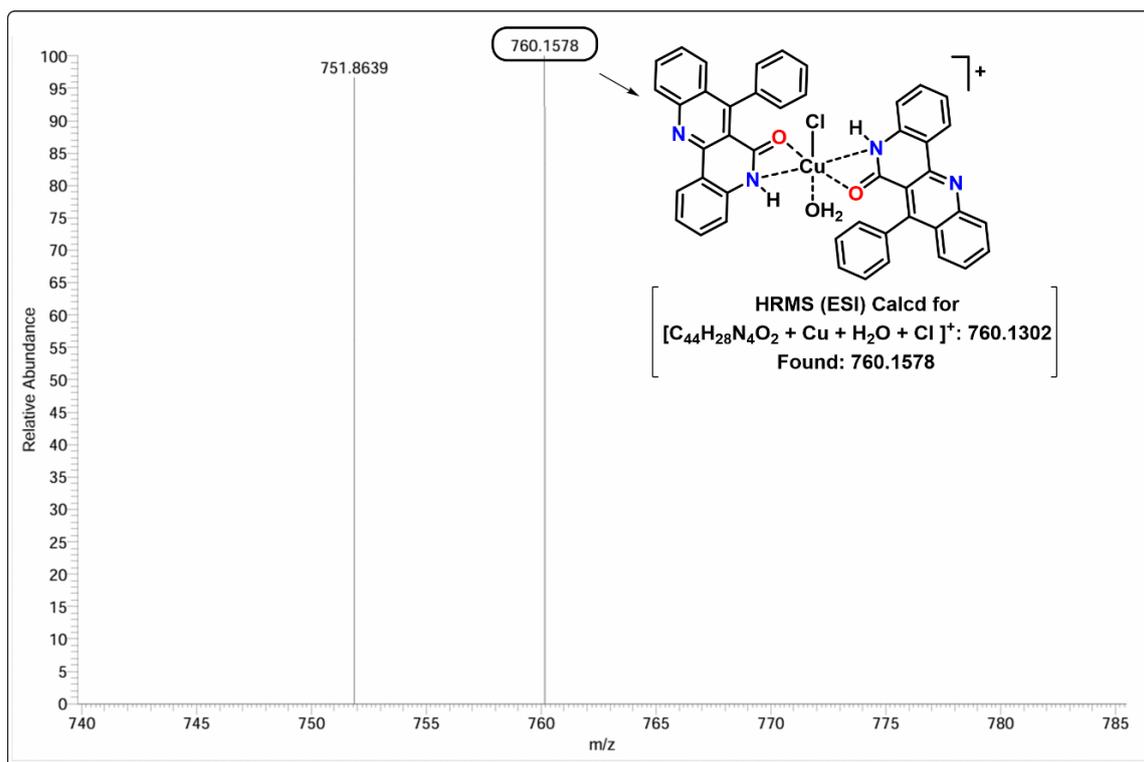


Fig. S6 HRMS spectra of possible probe **6**-Cu<sup>2+</sup> complexes

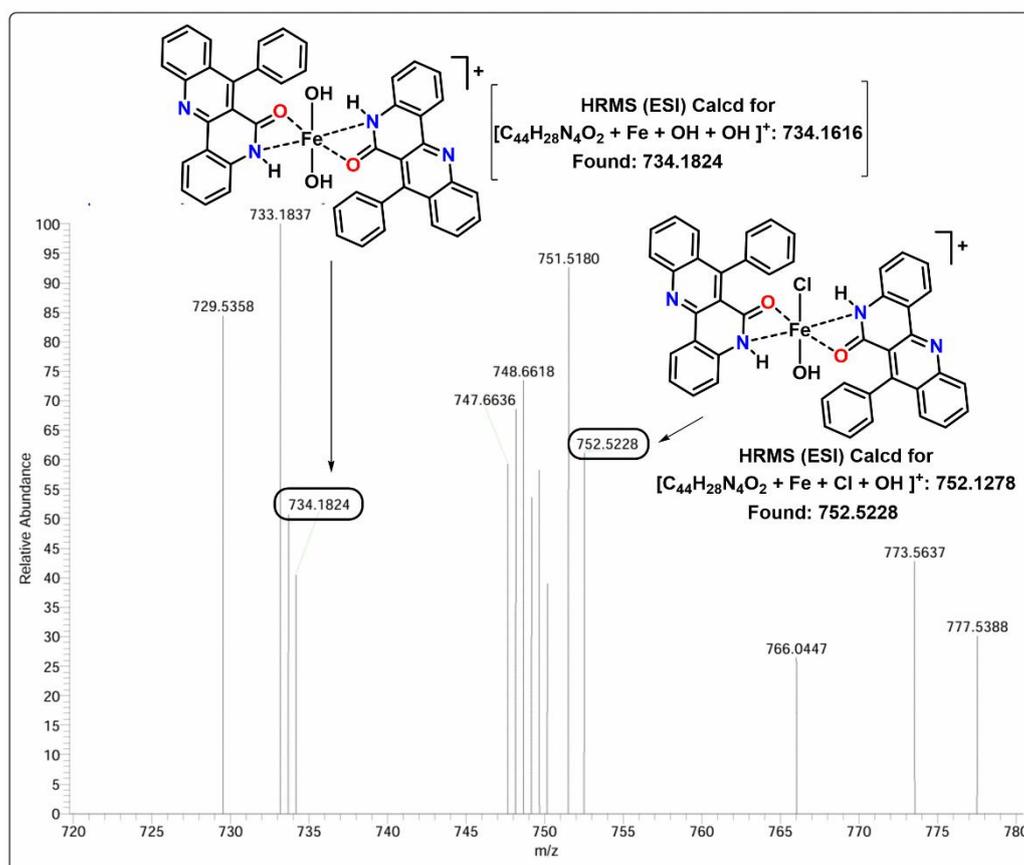


Fig. S7 HRMS spectra of possible probe **6**-Fe<sup>3+</sup> complexes

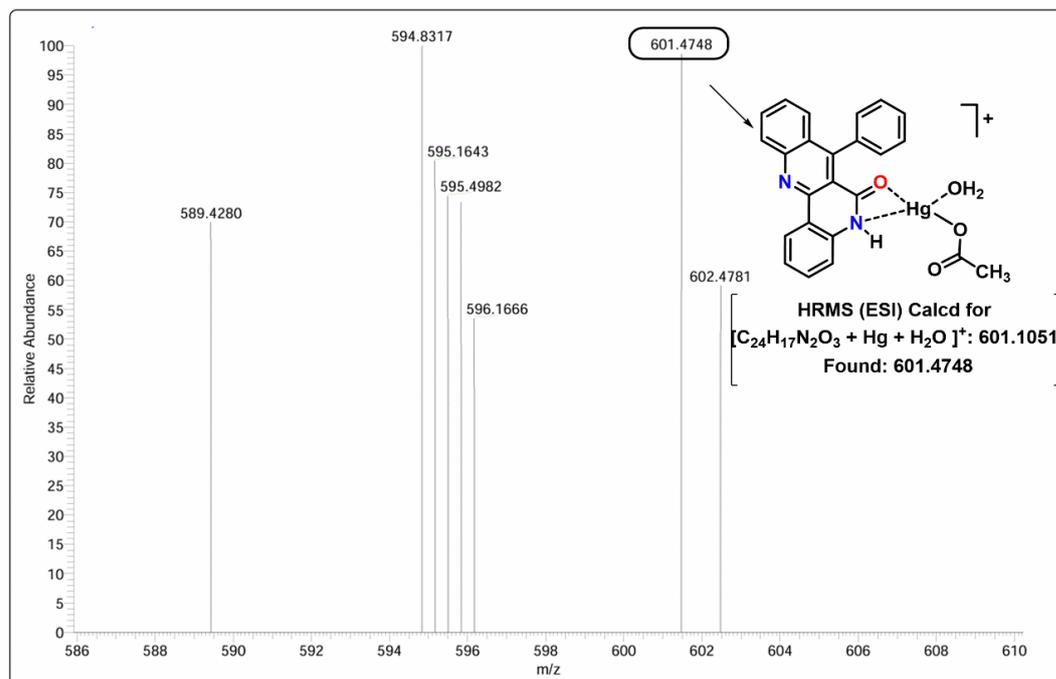


Fig. S8 HRMS spectra of possible probe **6**- $Hg^{2+}$  complexes

### 11. Reversibility of the fluorescence probe **6**:

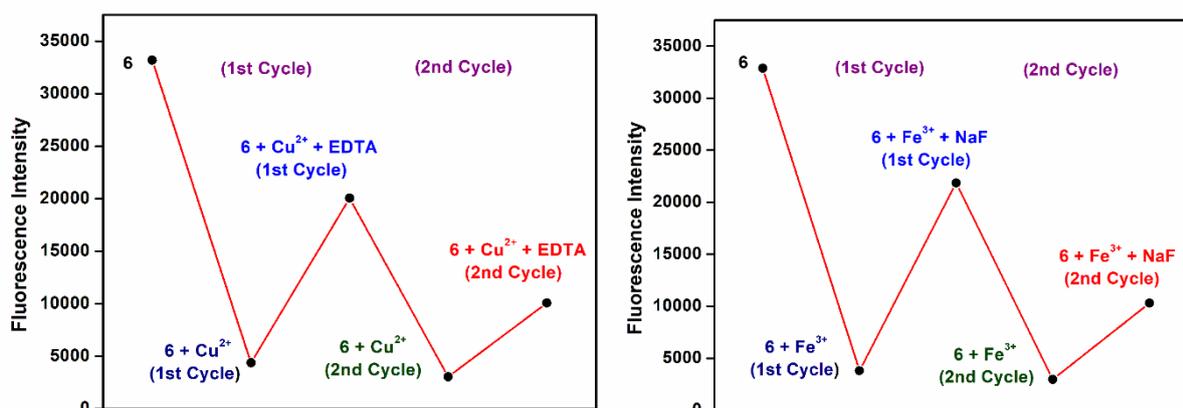


Fig. S9 Reversibility of probe **6** in presence of chelating ligands

## 12. Metal selectivity in presence of masking agents<sup>2</sup>

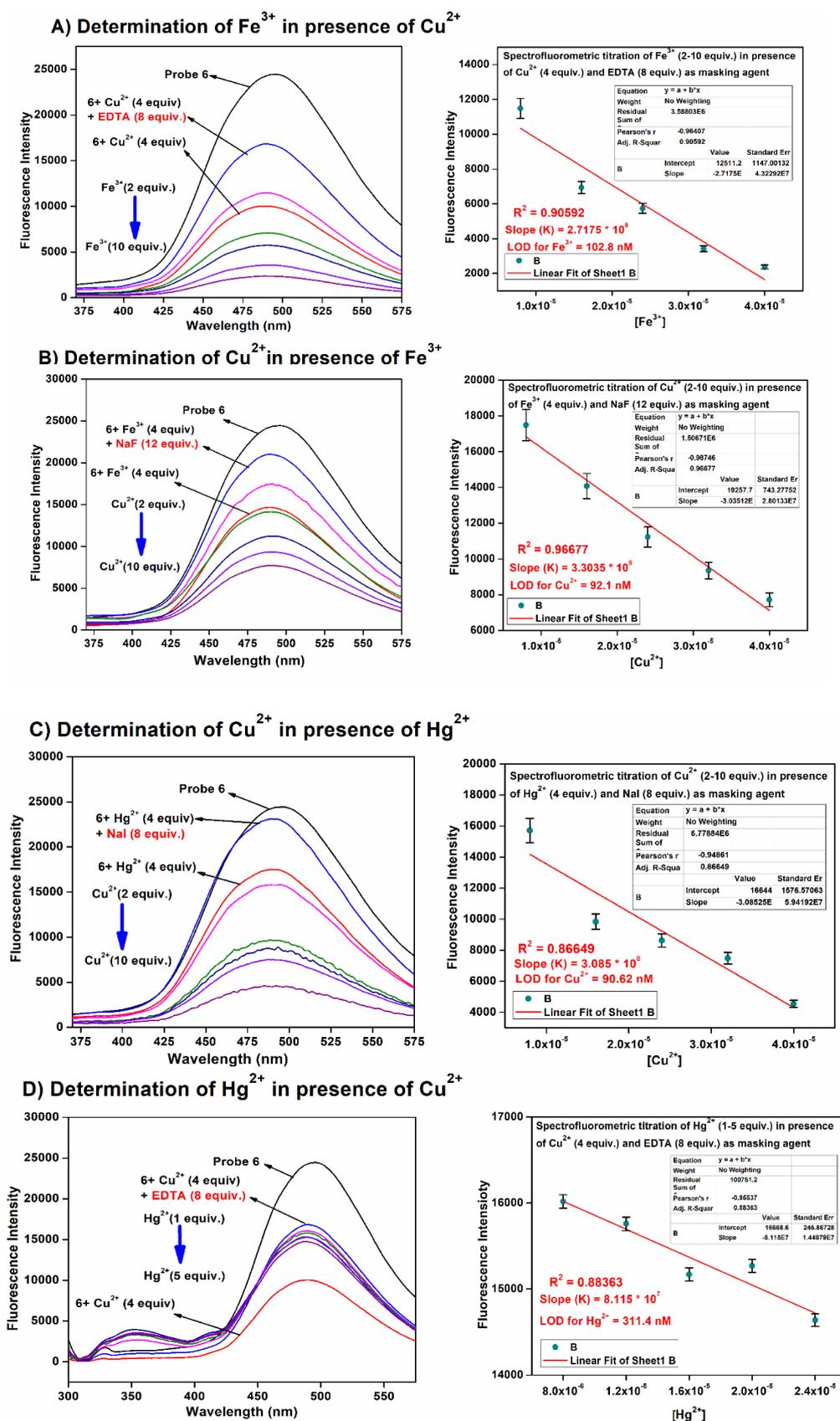
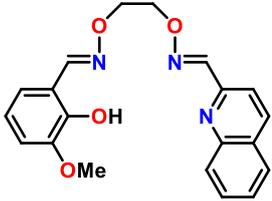
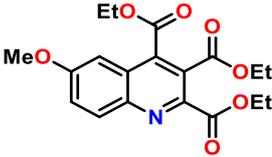
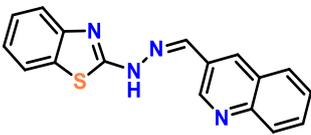
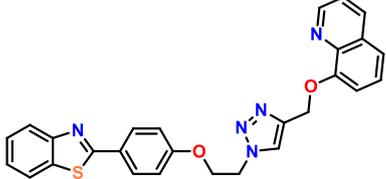
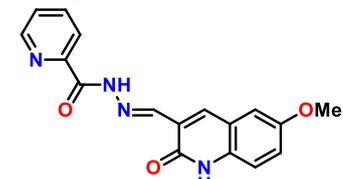
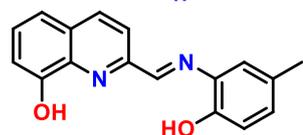
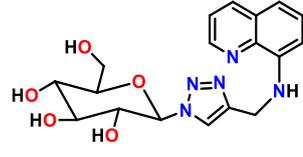
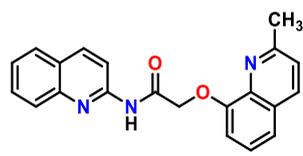
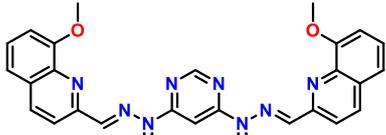
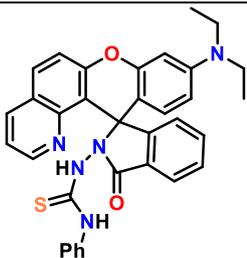
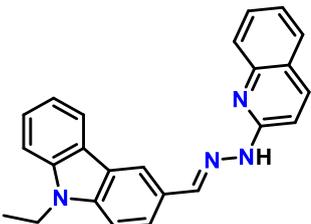
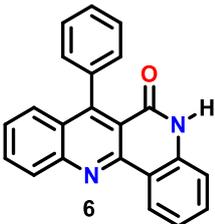


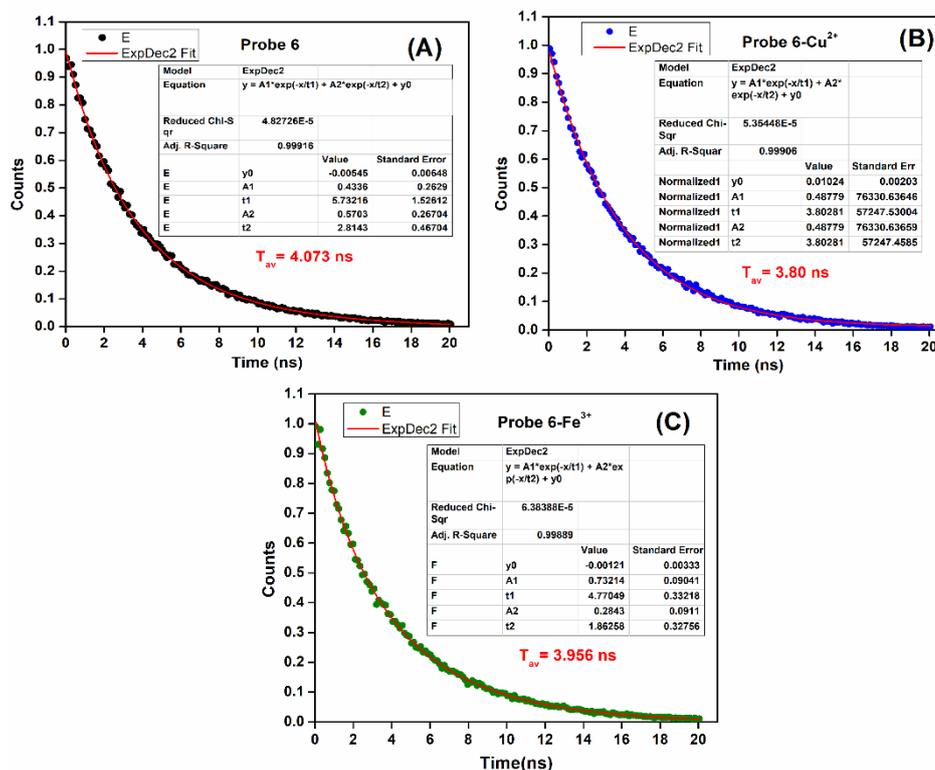
Fig. S10 Selectivity toward Cu<sup>2+</sup>, Fe<sup>3+</sup> and Hg<sup>2+</sup> in presence of masking agents

**13. Table S2. Comparison of the various quinoline and quinoline-2-one based chemosensors for the detection of Cu<sup>2+</sup>, Fe<sup>3+</sup> and Hg<sup>2+</sup> ions**

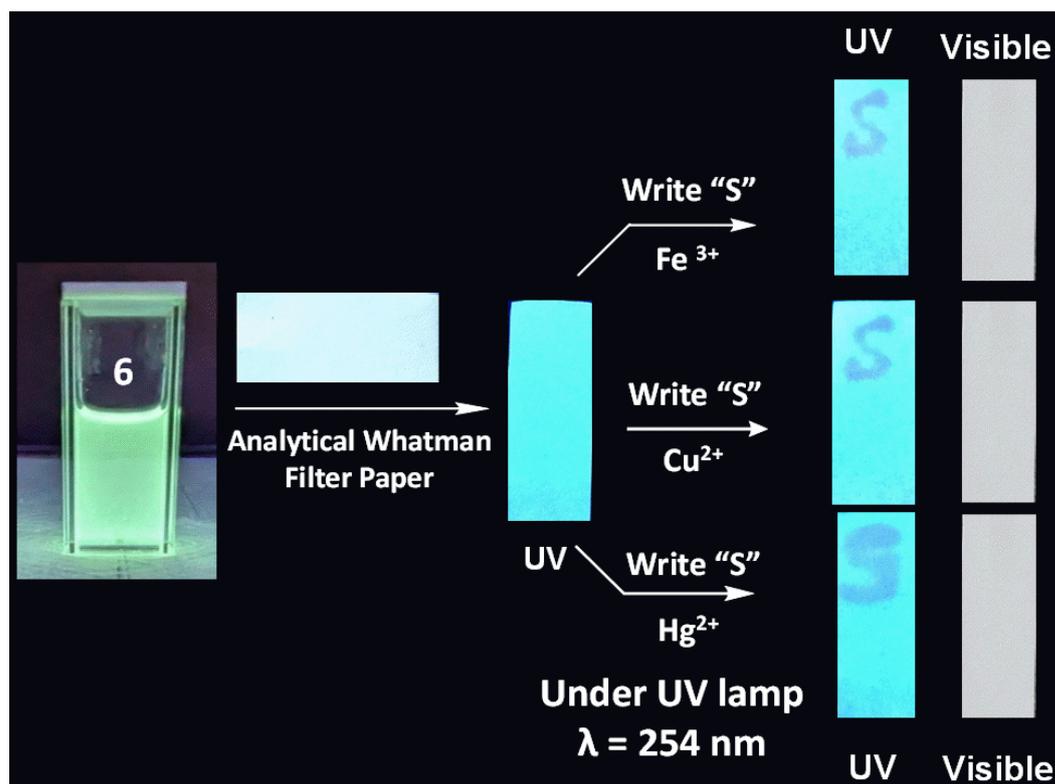
Sl. No.	Probe	Sensing metal ions	LOD (1 nM= 10 <sup>-9</sup> M)	Solvent system	Ref.
1		Fe <sup>3+</sup>	58 nM	H <sub>2</sub> O	3
2		Cu <sup>2+</sup>	301 nM	DMSO/H <sub>2</sub> O (2:8, v/v) HEPES buffer solution	4
3		Cu <sup>2+</sup>	115.3 nM	DMF-H <sub>2</sub> O (9:1 v/v)	5
4		Fe <sup>3+</sup>	640 nM	DMSO-HEPES buffer (10 mM, 1/1 v/v)	6
5		Cu <sup>2+</sup>	43.4 nM	CH <sub>3</sub> OH-H <sub>2</sub> O (1:2, v/v)	7
6		Cu <sup>2+</sup> & Fe <sup>3+</sup>	34 nM (Cu <sup>2+</sup> ); 47nM (Fe <sup>3+</sup> )	DMSO-H <sub>2</sub> O (1:1, v/v)	8
7		Cu <sup>2+</sup> & Ni <sup>2+</sup>	170 nM (Cu <sup>2+</sup> ); 180 nM (Ni <sup>2+</sup> )	DMSO-H <sub>2</sub> O (9:1, v/v) for Cu <sup>2+</sup> and CH <sub>3</sub> CN-H <sub>2</sub> O (9:1, v/v) for Ni <sup>2+</sup>	9
8		Cu <sup>2+</sup> & Fe <sup>3+</sup>	28 nM (Cu <sup>2+</sup> ); 73 nM (Fe <sup>3+</sup> )	i-PrOH	10
9		Fe <sup>3+</sup> , Al <sup>3+</sup> & Cu <sup>2+</sup>	91 nM (Fe <sup>3+</sup> ); 107 nM (Al <sup>3+</sup> ); 1580 nM (Cu <sup>2+</sup> )	CH <sub>3</sub> CN-H <sub>2</sub> O (9:1, v/v)	11

10		Hg <sup>2+</sup>	8.6 nM	H <sub>2</sub> O	12
11		Fe <sup>3+</sup>	86.7 μM or 86700 nM	DMF- HEPES- NaOH buffer solution (1:1 v/v)	13
12		Hg <sup>2+</sup>	25.9 nM	CH <sub>3</sub> CN-H <sub>2</sub> O (1:1, v/v)	14
13		Cu <sup>2+</sup> , Fe <sup>3+</sup> and Hg <sup>2+</sup>	52.5 nM (Cu <sup>2+</sup> ); 34.88 nM (Fe <sup>3+</sup> ) and 16.5 nM (Hg <sup>2+</sup> )	DMSO-H <sub>2</sub> O (8:2, v/v)	<b>This Work</b>

#### 14. Fluorescence Lifetime calculations (TCSPC) of Probe 6 with metal ions



## 15. Application of fluorescence probe in encryption ink



## 16. Notes and references

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