

**Electronic supplementary information**

**Synthesis and spectral properties of 8-anilinonaphthalene-1-sulfonic acid (ANS) derivatives prepared by microwave-assisted copper(0)-catalyzed Ullmann reaction**

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# Supporting Information

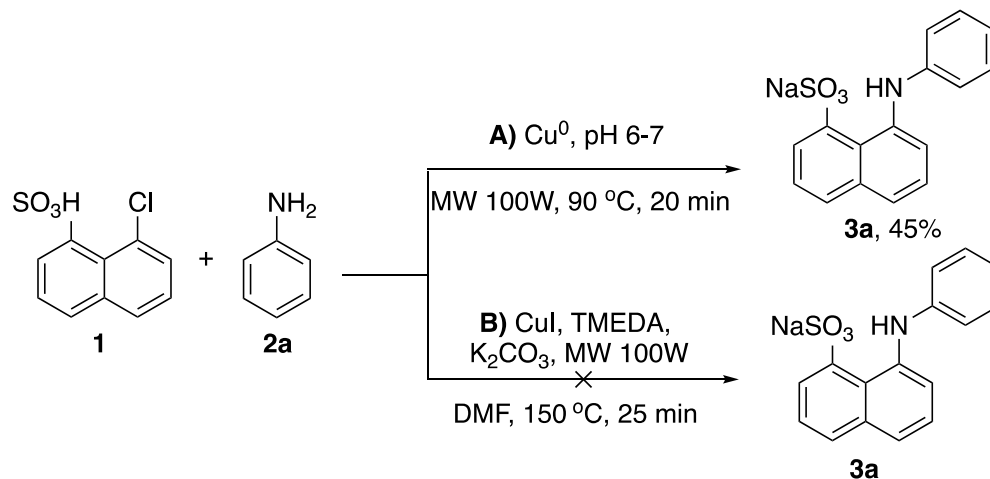
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## I. Method optimization

Scheme S1



We initially investigated two Ullman coupling conditions for reacting 8-chloronaphthalene-1-sulfonic acid with aniline (Scheme S1 and Table S1).

**Method A:**<sup>1-3</sup> To 8-chloronaphthalene-1-sulfonic acid (**1**, 1 equiv), elemental copper (cat. amount), and aniline (**2a**, 2 equiv) in  $\text{H}_2\text{O}$ , were added  $\text{NaH}_2\text{PO}_4$  and  $\text{Na}_2\text{HPO}_4$  to adjust the pH to 6-7. Then the reaction was conducted under microwave conditions at 90 °C for 20 min.

**Method B:**<sup>4, 5</sup> To **1** (1 equiv) in DMF, were added tetramethylethylenediamine (TMEDA, cat. amount), CuI (cat. amount),  $\text{K}_2\text{CO}_3$  (1.5 equiv) and aniline (2 equiv). Then the reaction was conducted under microwave conditions at 150 °C for 25 min.

Method A resulted in a 45% isolated yield of **3a** and no product was obtained from method B. Therefore, we next optimized method A by screening copper catalysts, the amount of aniline, reaction time, and temperature (summarized in the table below). The optimized conditions are as follows: reaction in the presence of **1** (0.41 mmol, 1 equiv), **2a** (0.46 mmol, 1.1 equiv) and a catalytic amount copper element (10 mol%) in a buffer solution (pH 6-7) of  $\text{Na}_2\text{HPO}_4$  (pH 9.6) and  $\text{NaH}_2\text{PO}_4$  (pH 4.2) for 1 h at 100 °C under microwave (100 W) conditions, through which the yield of **3a** was improved to 63%.

**Table S1. Reaction optimization**

Clc1ccc(S(=O)(=O)O)cc1 (**1**) + Nc1ccccc1 (**2a**)
   
 1) Catalyst, pH 6-7  
 MW, Temp  
 2) NaOH adjust pH > 12
   
Nc1ccc(S(=O)(=O)[O-])cc1 (**3a,b**)

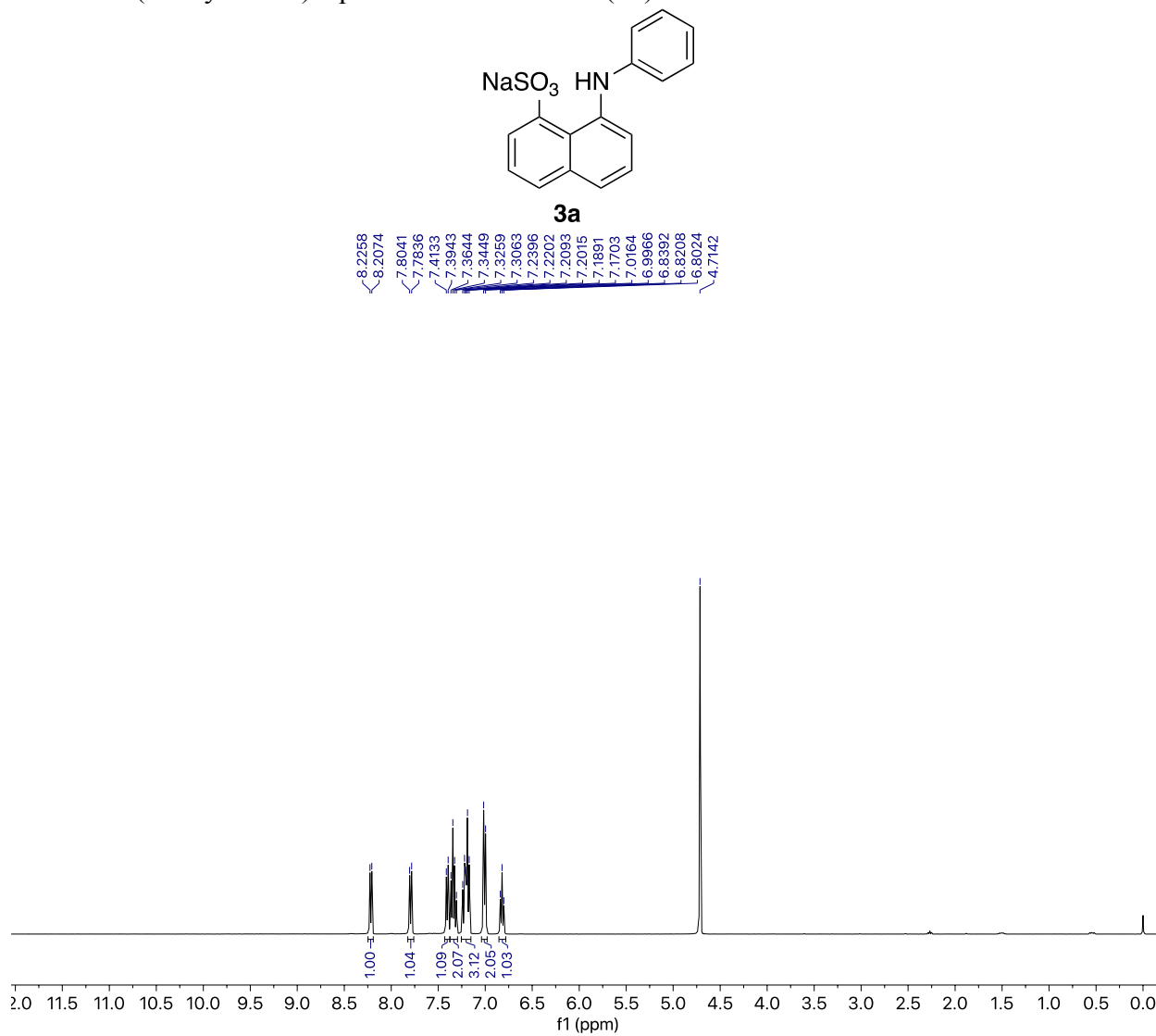
Entry	Catalyst (mol %)	Equiv of aniline	Temp (° C)	Reaction time	Yield (%) <sup>b</sup>
1	CuI (10)	1.1	80	1 h	trace
2	CuCl (10)	1.1	80	1 h	trace
3	Cu <sup>0</sup> (10)	1.1	80	1 h	47
4	Cu <sup>0</sup> (15)	1.1	80	1 h	47
5	Cu <sup>0</sup> (10)	2	80	1 h	47
7	Cu <sup>0</sup> (10)	1.1	100	1 h	53
8	Cu <sup>0</sup> (10)	1.1	120	1 h	52
10	Cu <sup>0</sup> (10)	1.1	100	1.5 h	63
11	Cu <sup>0</sup> (10)	1.1	100	2 h	63

<sup>a</sup>Reaction was carried out in 5 ml sealed microwave tube. **1** (0.41 mmol, 1 equiv), **2a** and catalyst were added into a buffer solution (pH 6-7) of Na<sub>2</sub>HPO<sub>4</sub> and NaH<sub>2</sub>PO<sub>4</sub> and irradiated by microwave (100 W).

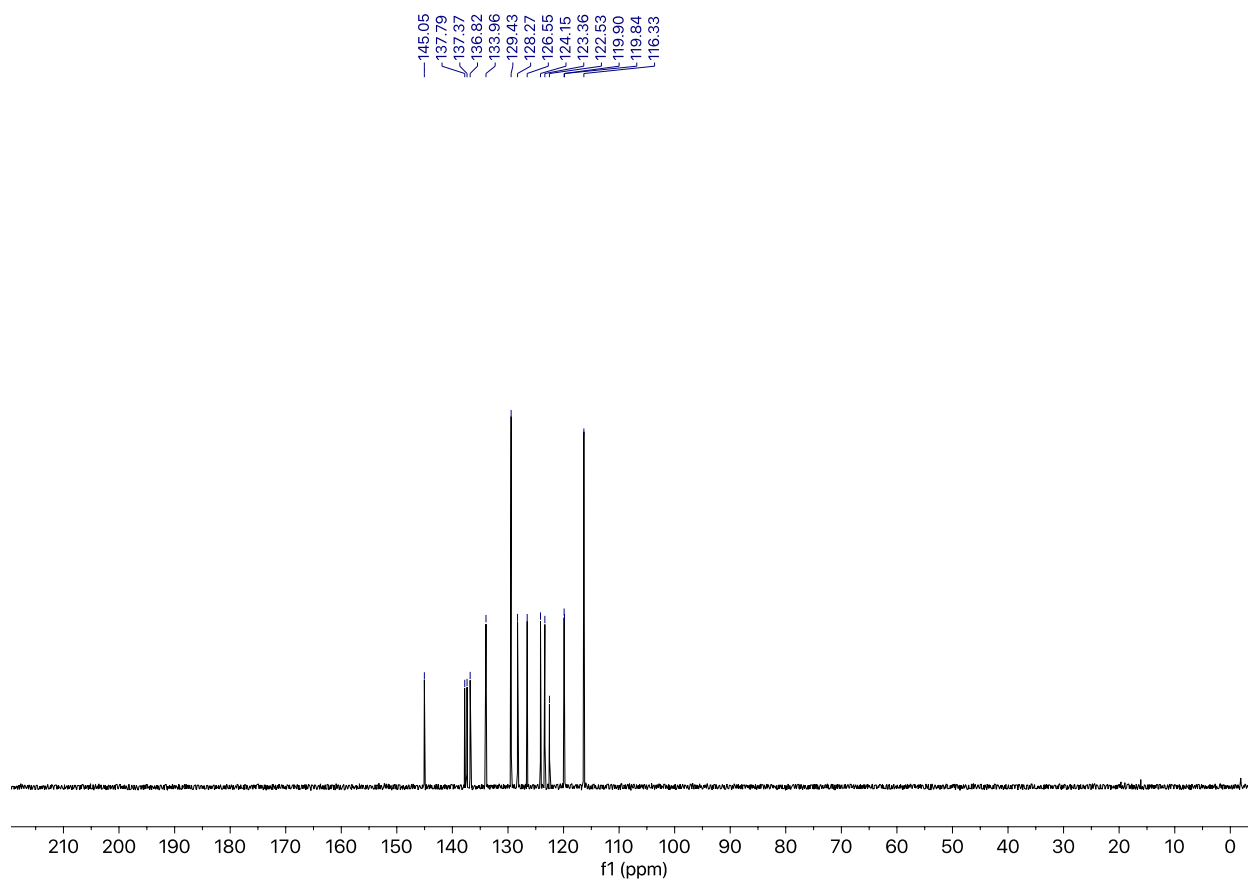
<sup>b</sup>Isolated yields.

## II. Spectra of analogs

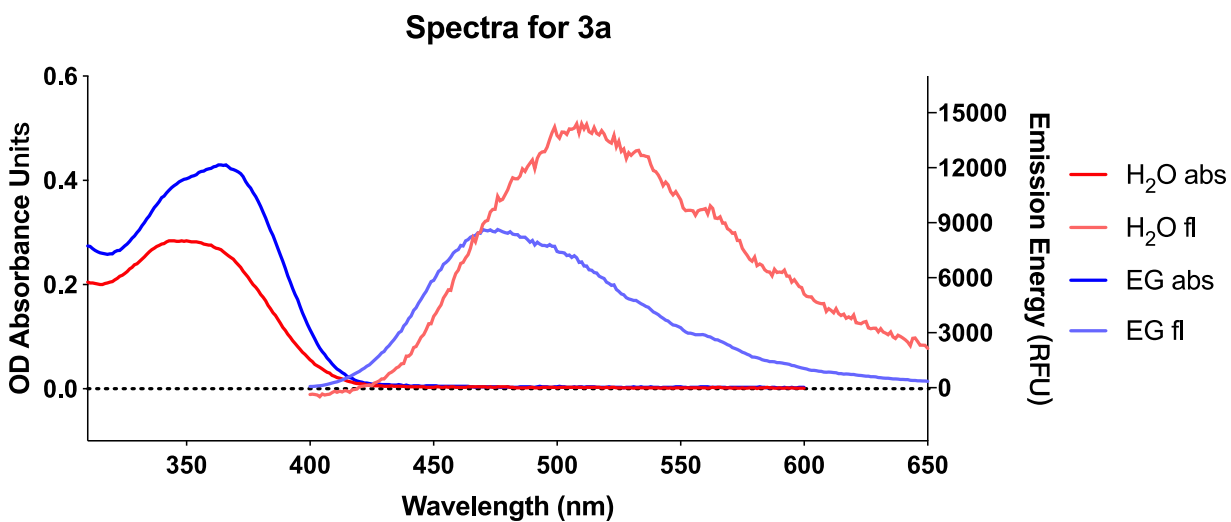
Sodium 8-(Phenylamino)naphthalene-1-sulfonate (**3a**)



**Figure S1.** Proton NMR for **3a**.



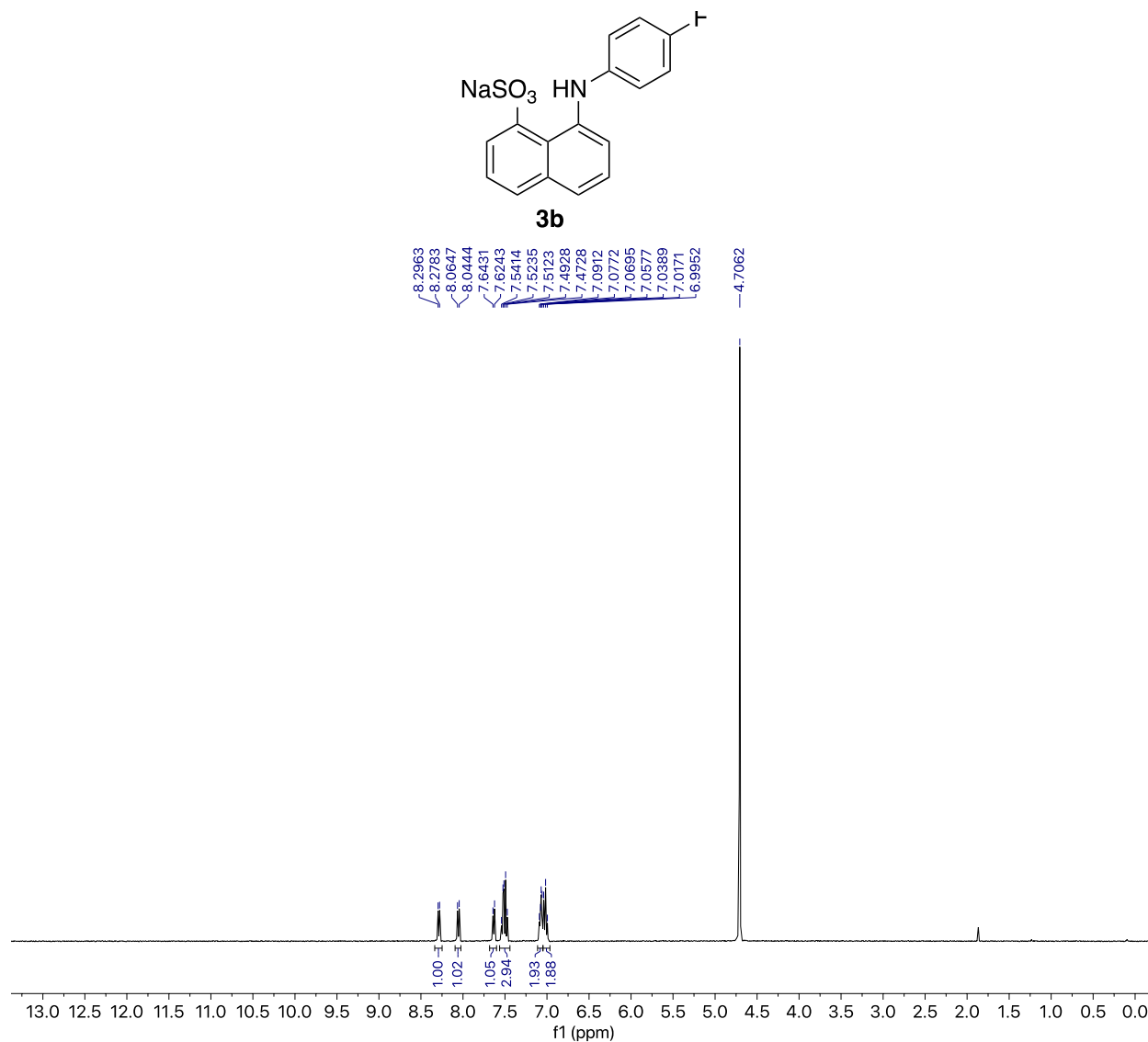
**Figure S2.** Carbon NMR for **3a**.



\*Fluorescence spectrum in ethylene glycol was taken at a lower gain to achieve an emission spectrum within the measurement parameters of the instrument.

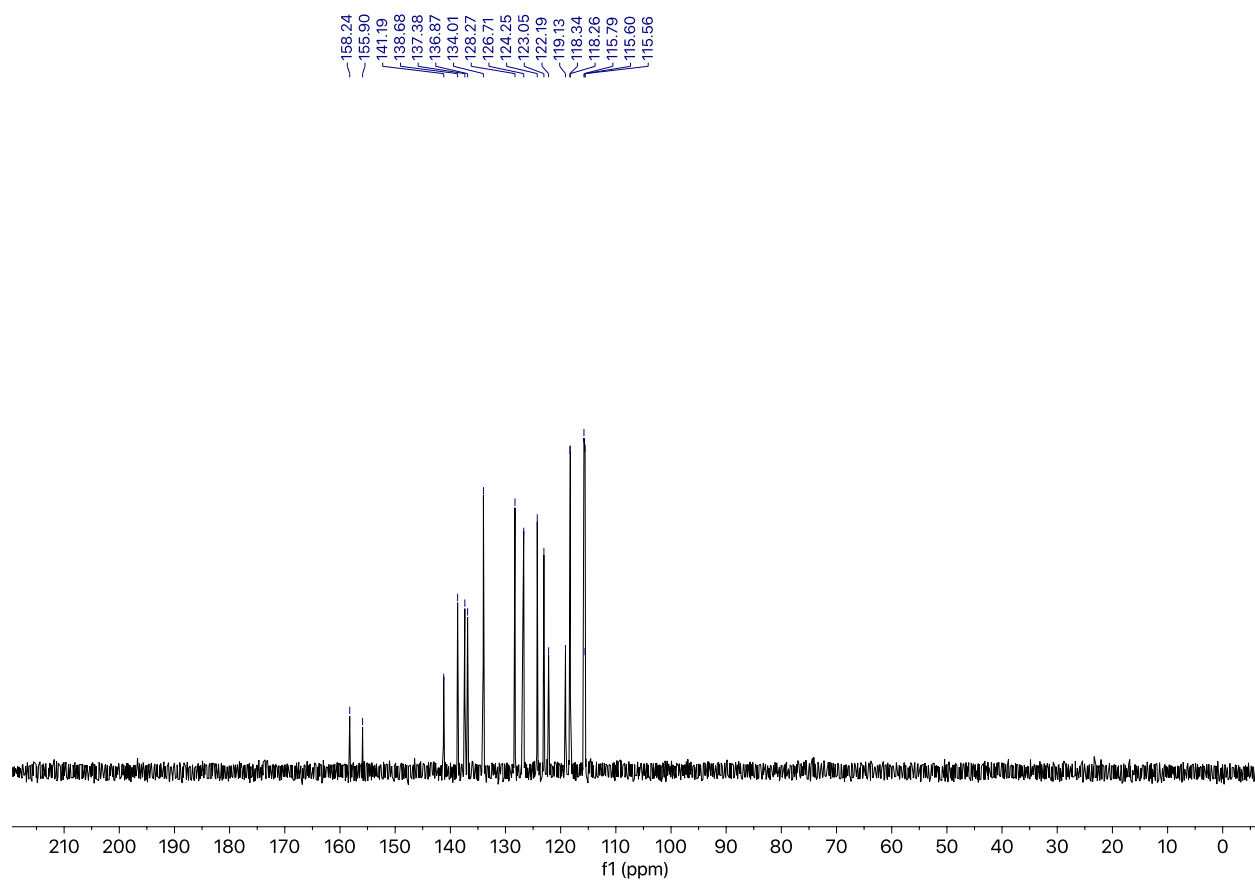
**Figure S3.** Fluorescent spectra for **3a**.

Sodium 8-((4-Fluorophenyl)amino)naphthalene-1-sulfonate (**3b**)

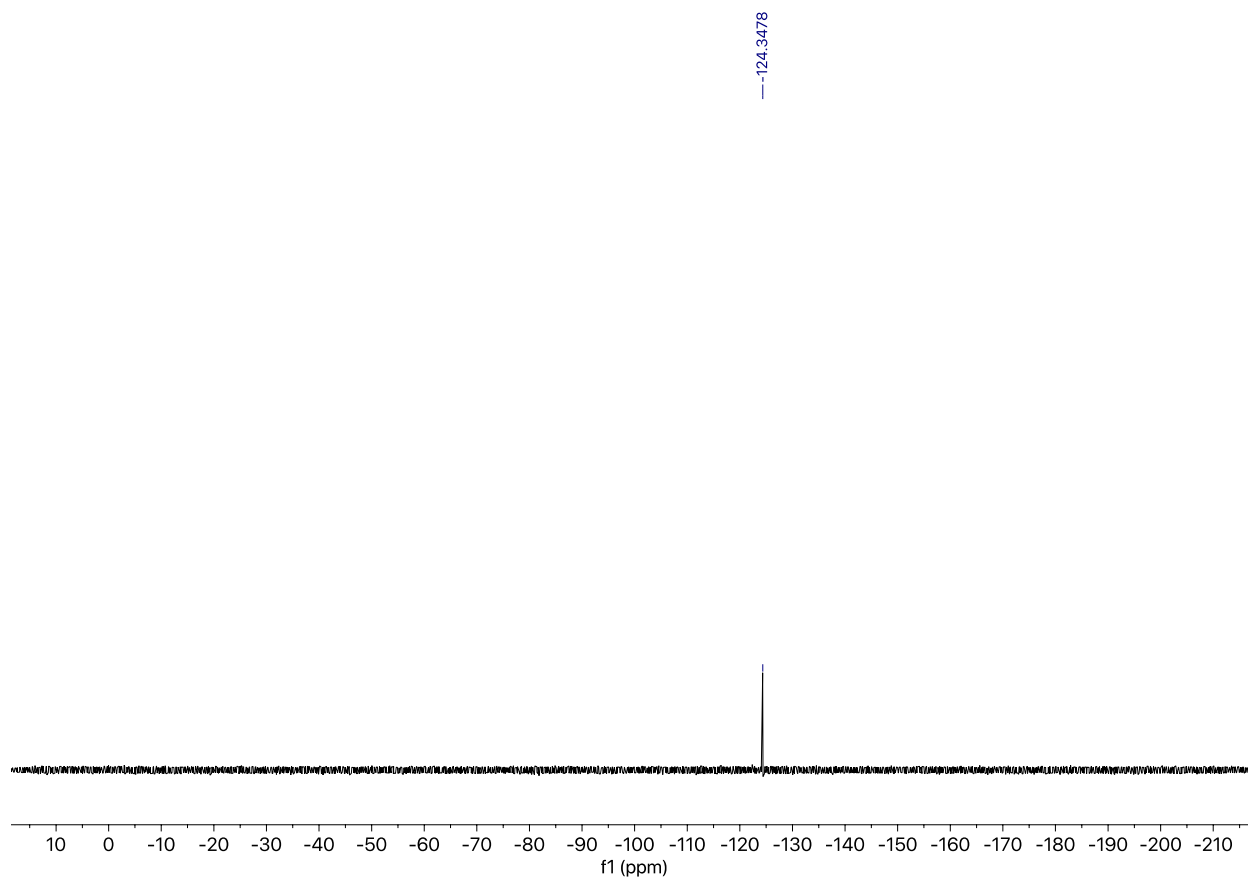


**Figure S4.** Proton NMR for **3b**.

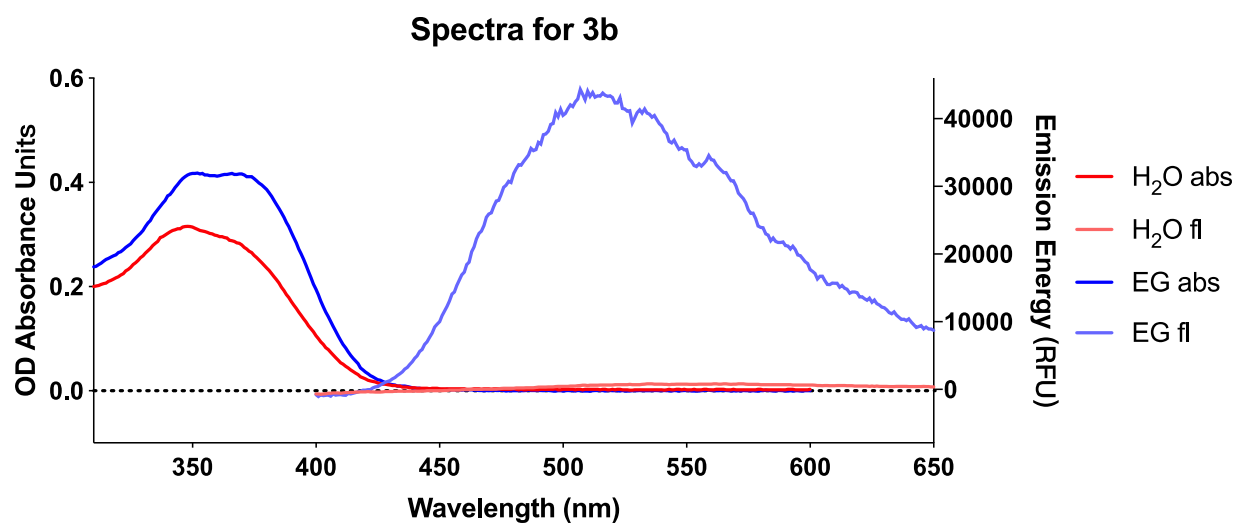




**Figure S5.** Carbon NMR for **3b**.

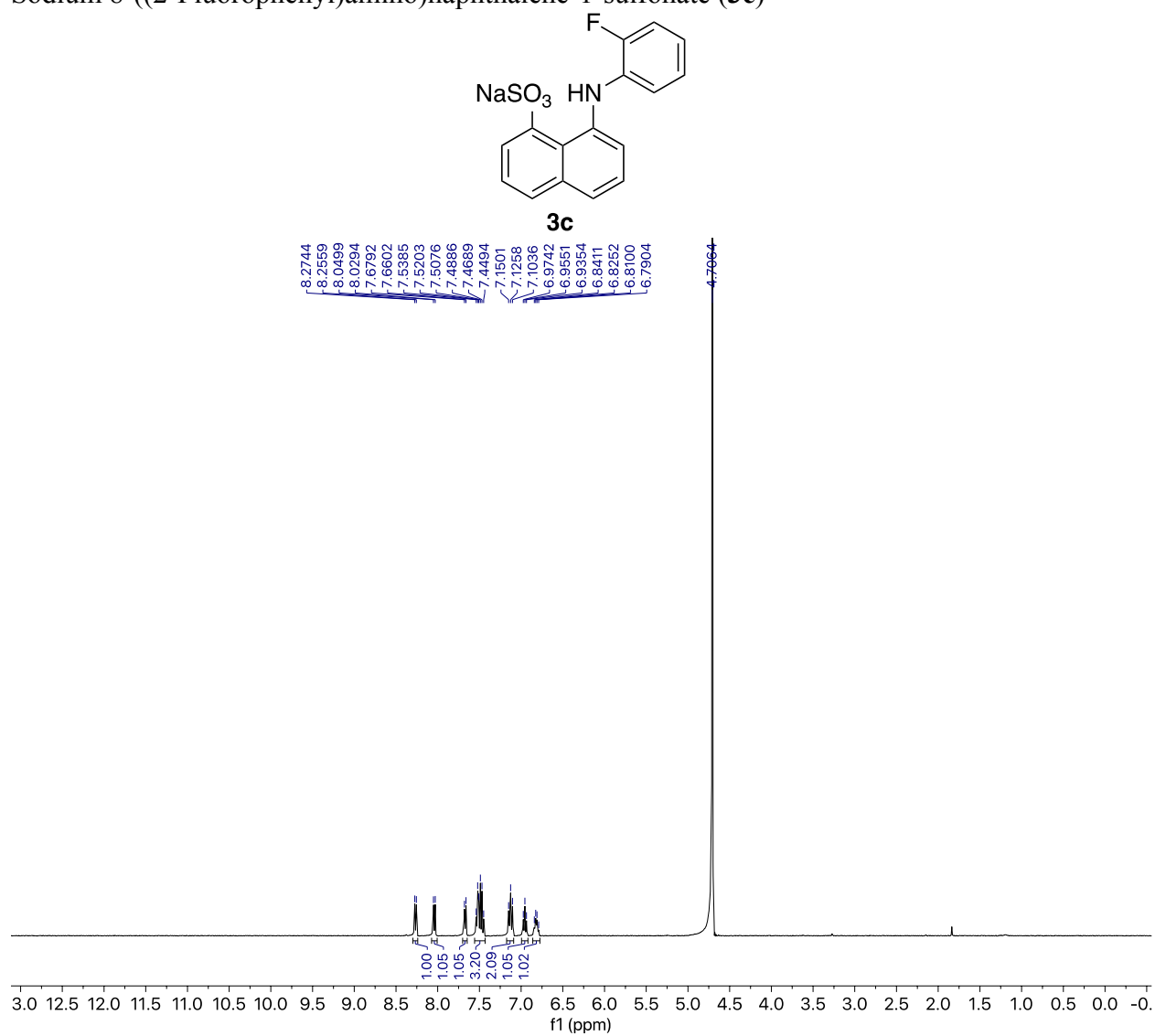


**Figure S6.** Fluorine NMR for **3b**.

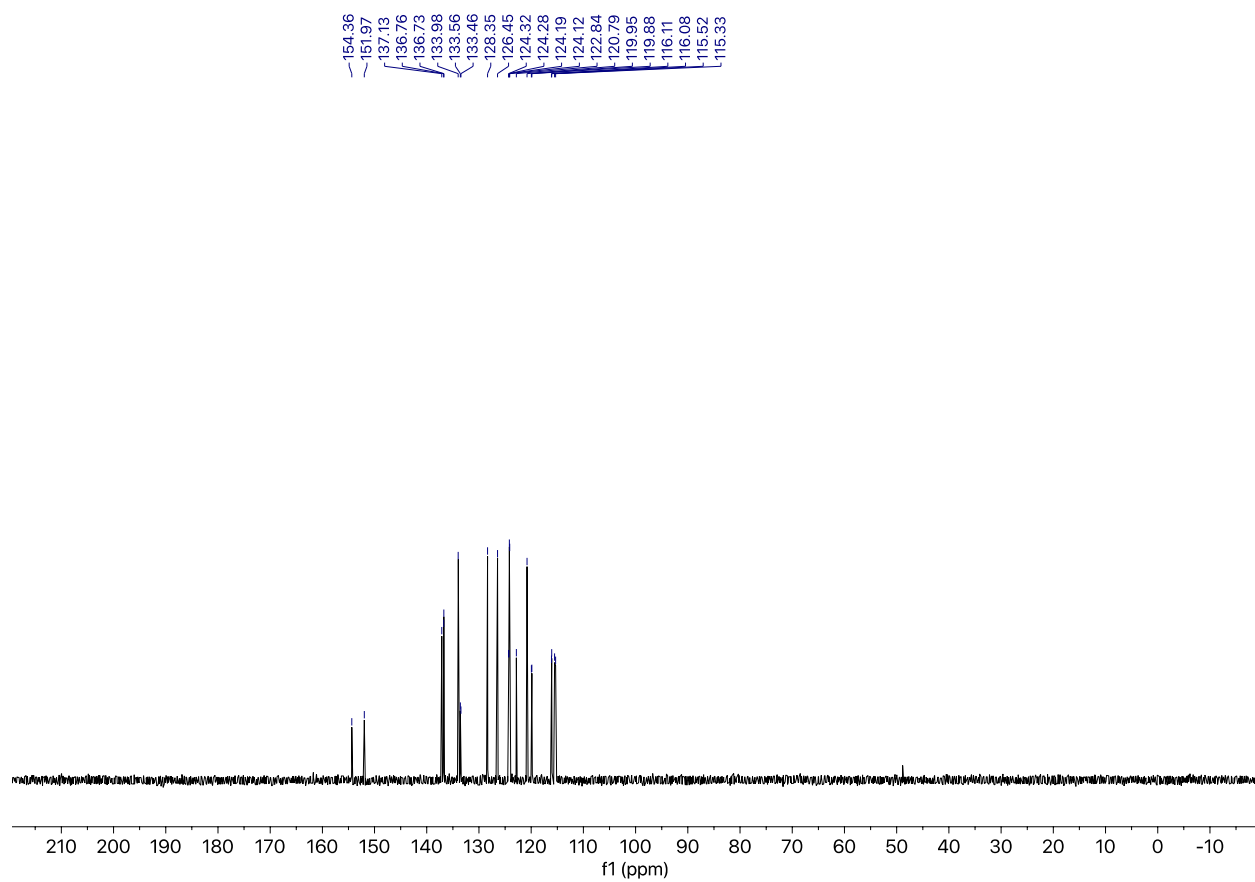


**Figure S7.** Fluorescent spectra for **3b**.

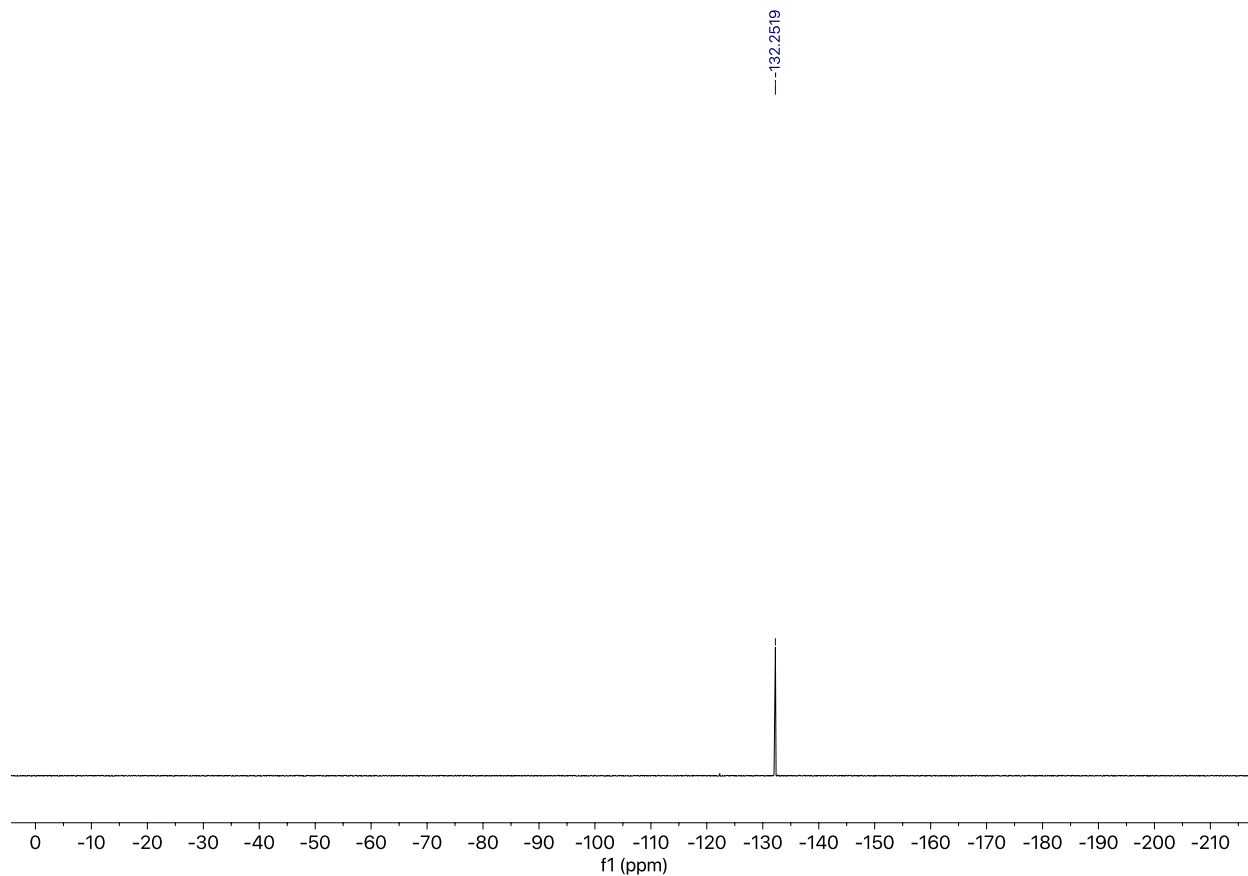
Sodium 8-((2-Fluorophenyl)amino)naphthalene-1-sulfonate (**3c**)



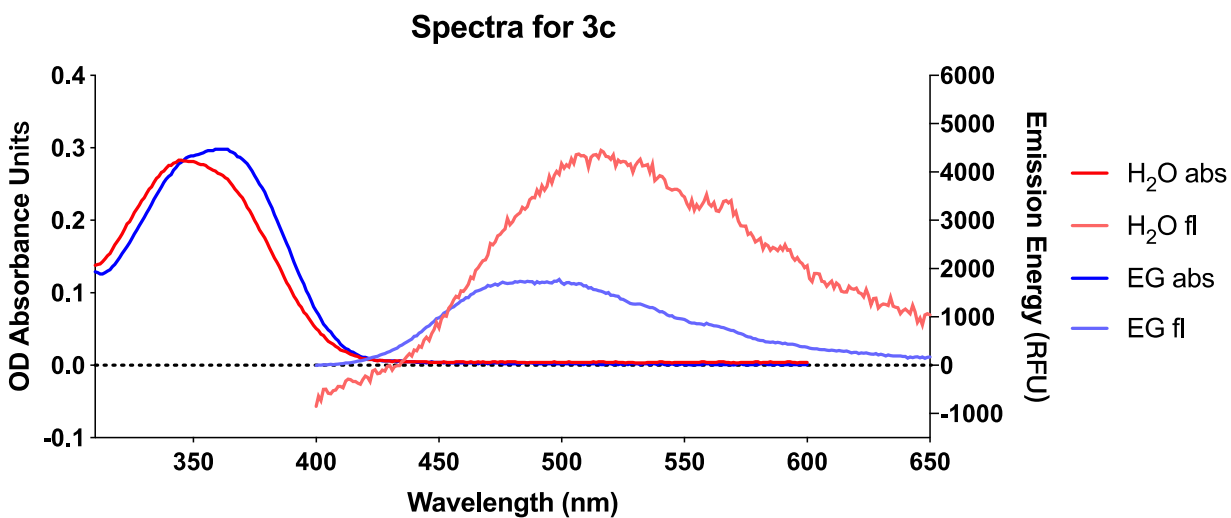
**Figure S8.** Proton NMR for **3c**.



**Figure S9.** Carbon NMR for **3c**.



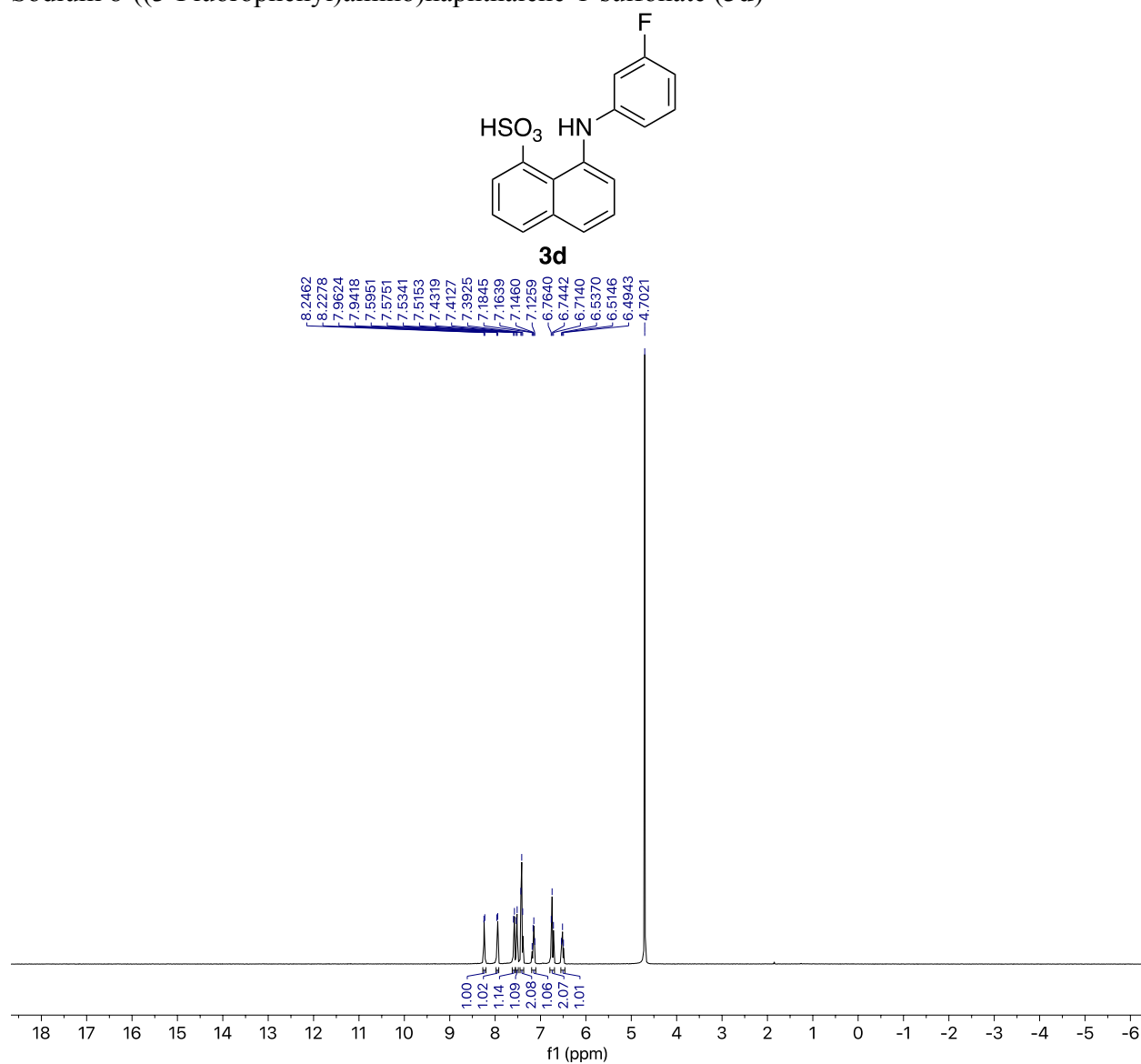
**Figure S10.** Fluorine NMR for **3c**.



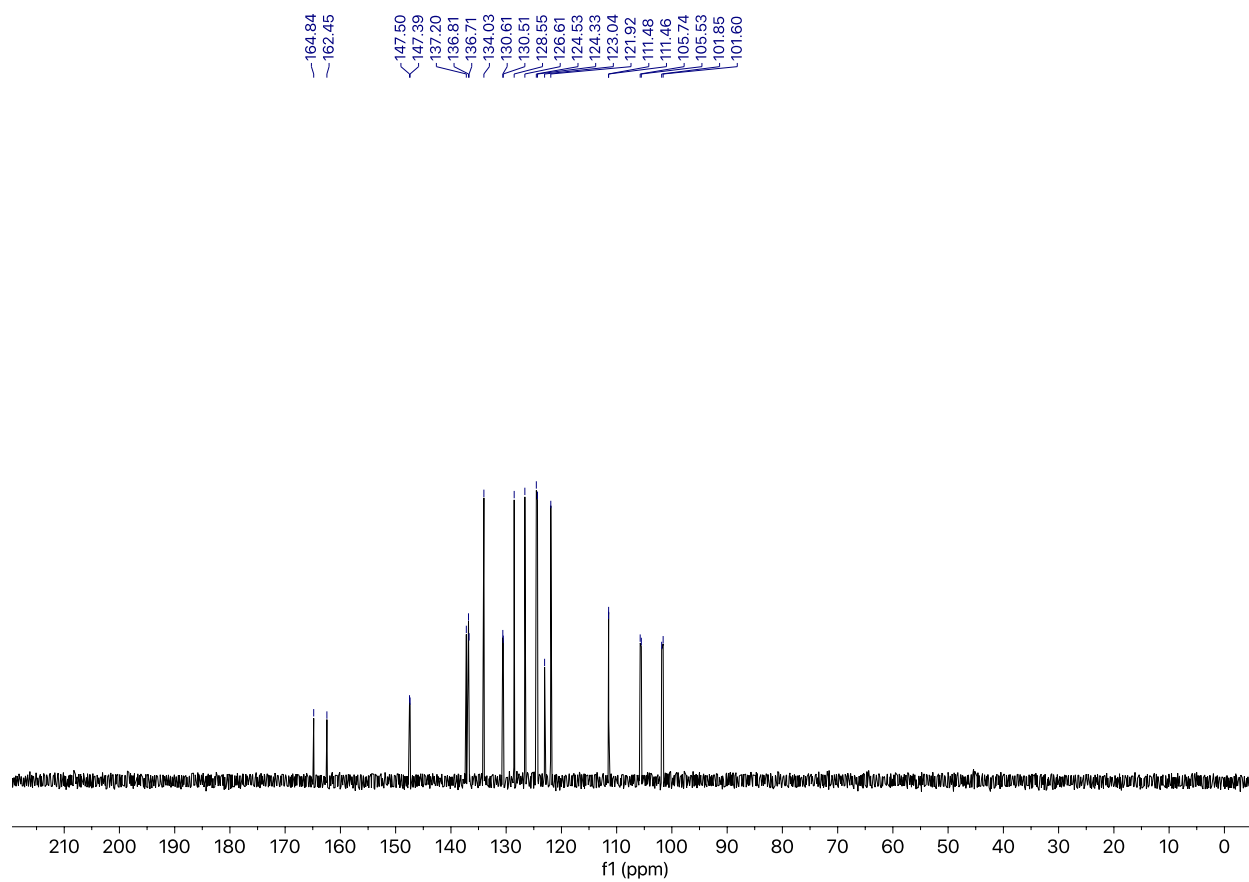
\*Fluorescence spectrum in ethylene glycol was taken at a lower gain to achieve an emission spectrum within the measurement parameters of the instrument.

**Figure S11.** Fluorescent spectra for **3c**.

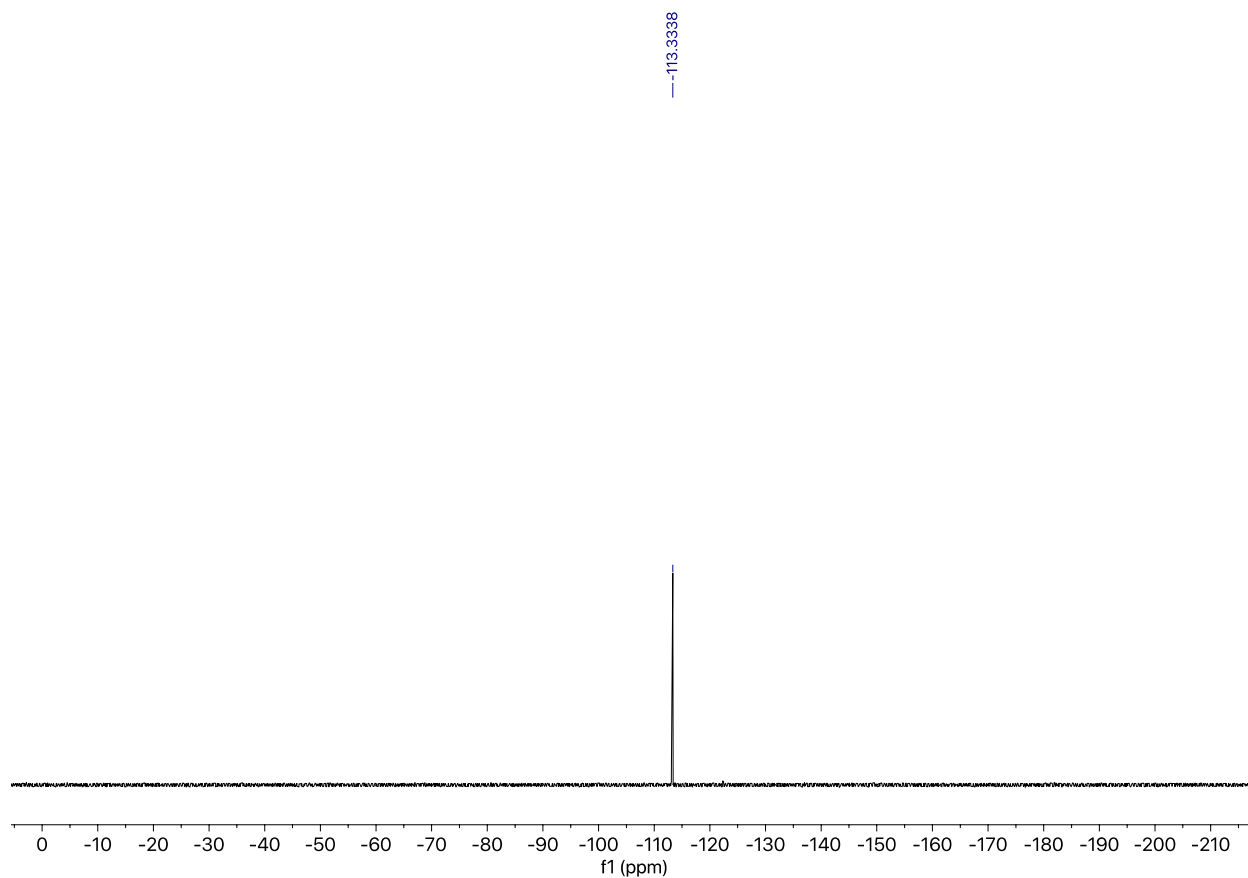
Sodium 8-((3-Fluorophenyl)amino)naphthalene-1-sulfonate (**3d**)



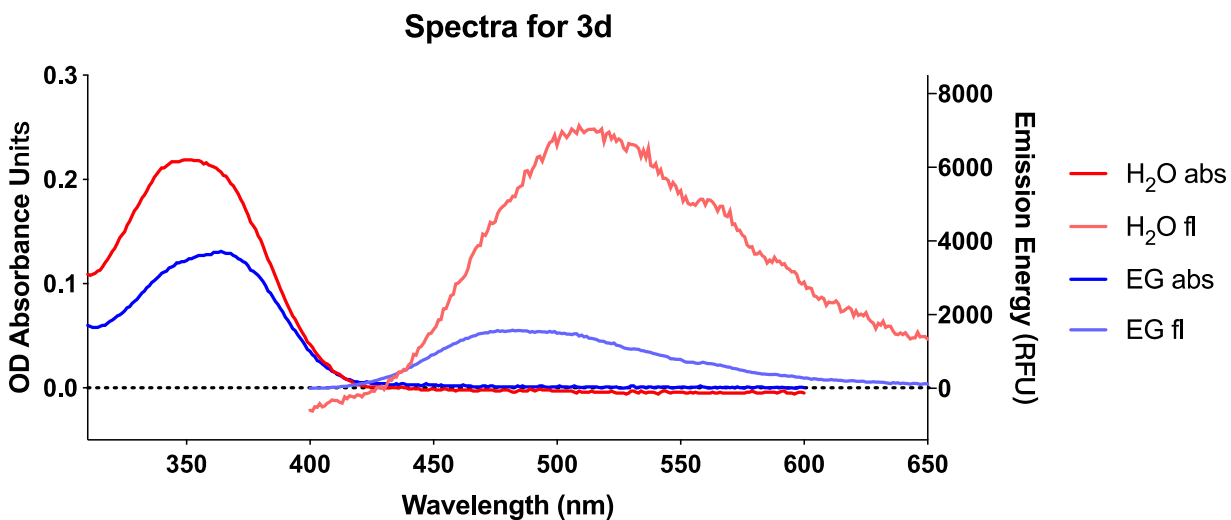
**Figure S12.** Proton NMR for **3d**.



**Figure S13.** Carbon NMR for **3d**.



**Figure S14.** Fluorine NMR for **3d**.

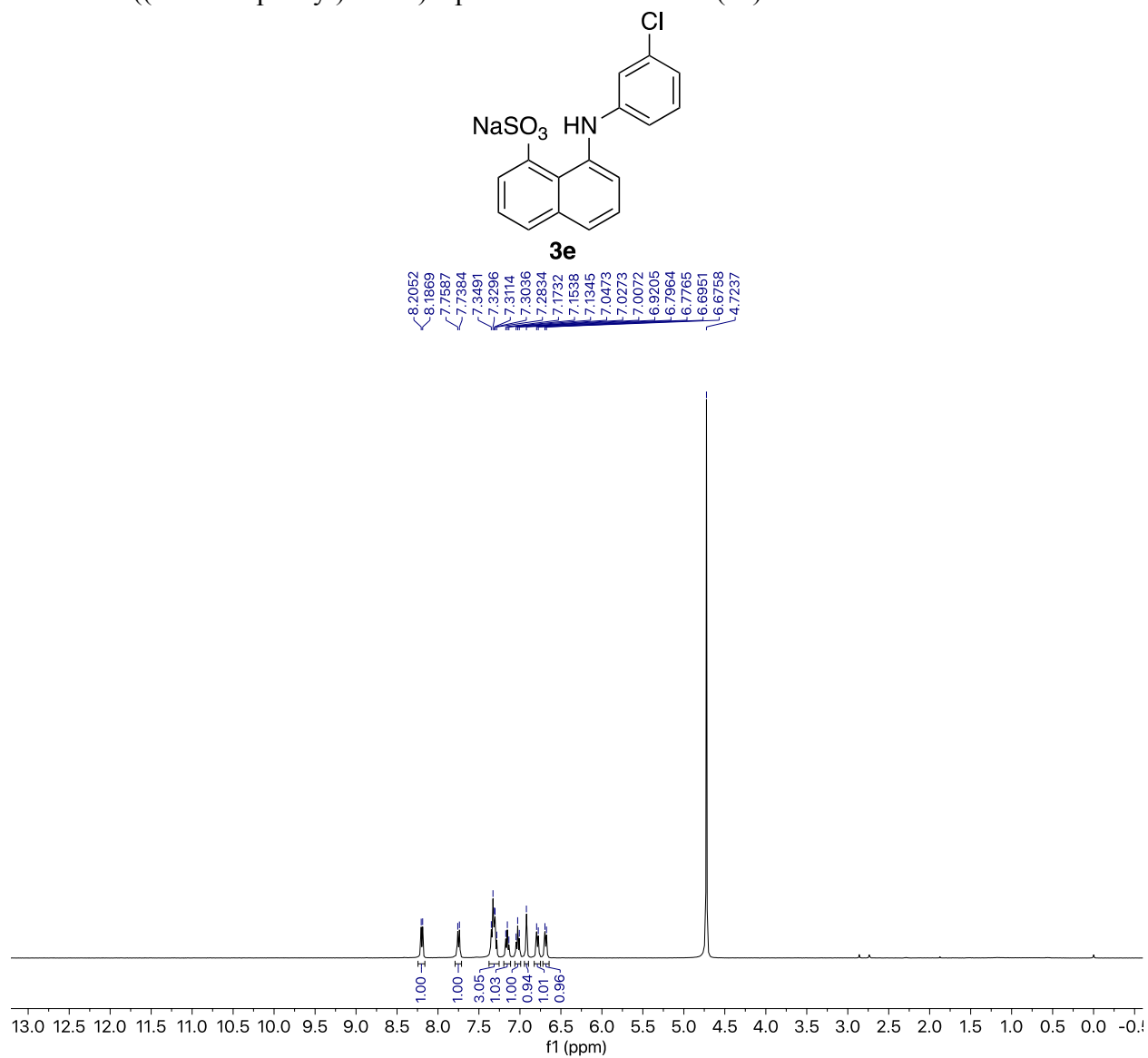


\*Fluorescence spectrum in ethylene glycol was taken at a lower gain to achieve an emission spectrum within the measurement parameters of the instrument.

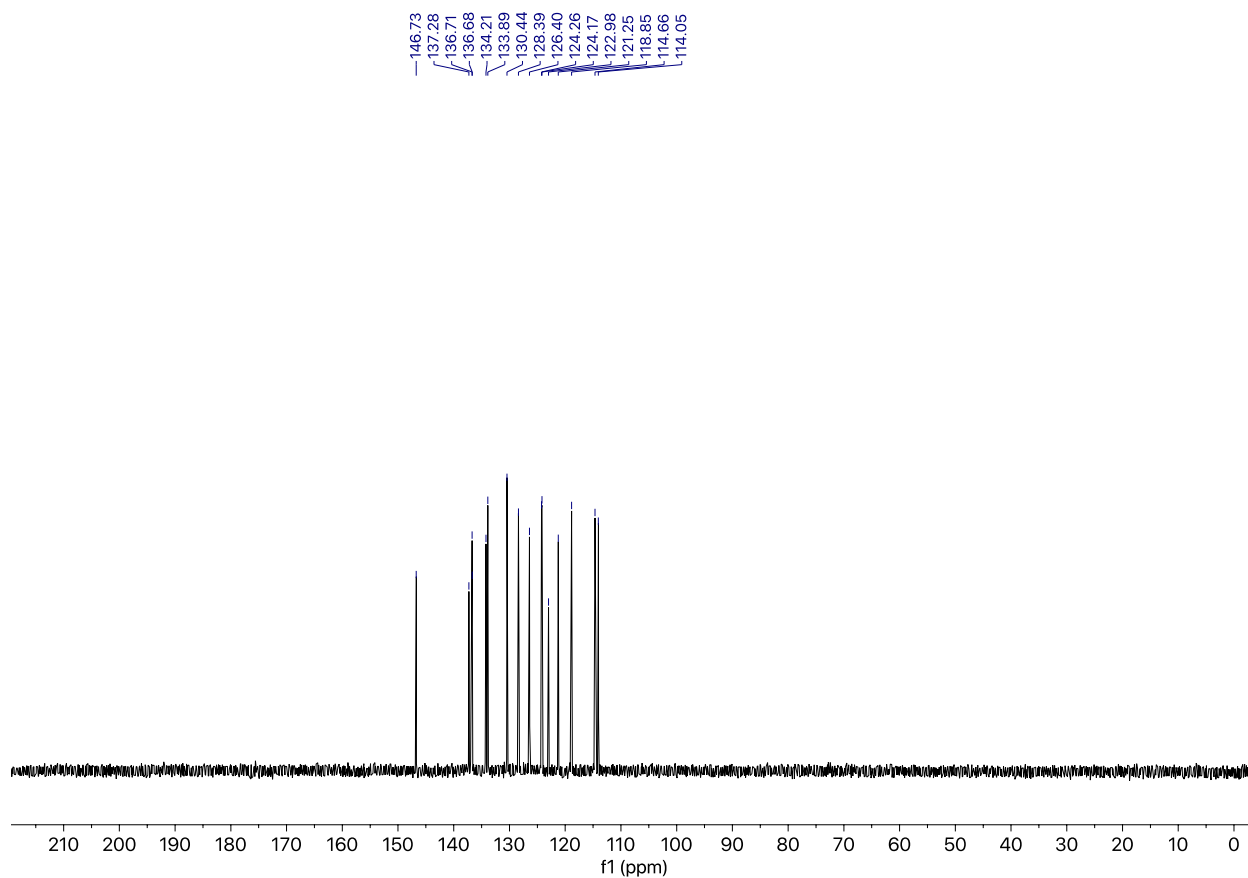
**Figure S15.** Fluorescent spectra for **3d**.



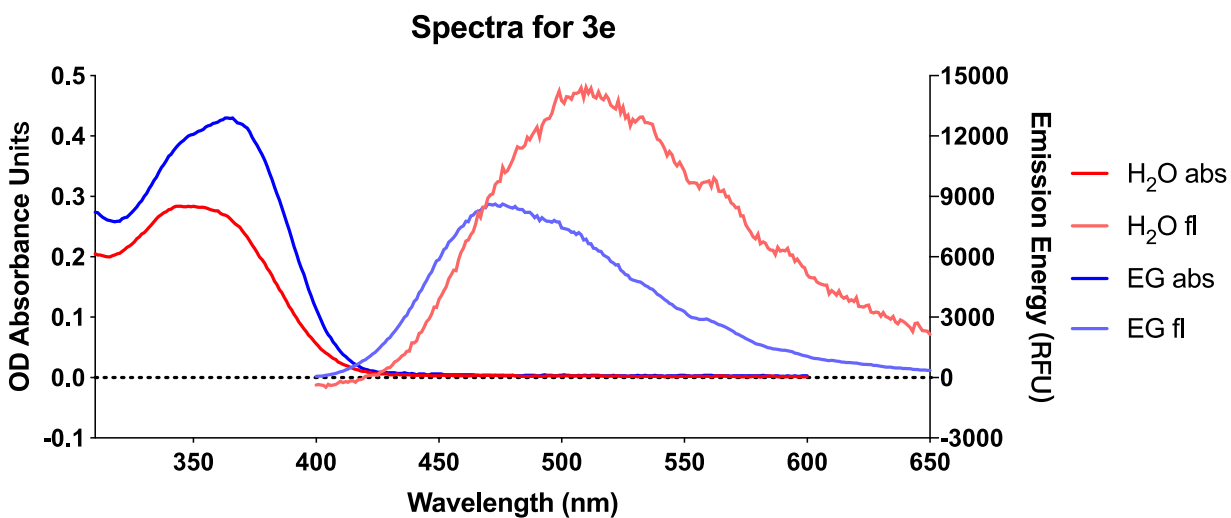
Sodium 8-((3-Chlorophenyl)amino)naphthalene-1-sulfonate (**3e**)



**Figure S16.** Proton NMR for **3e**.



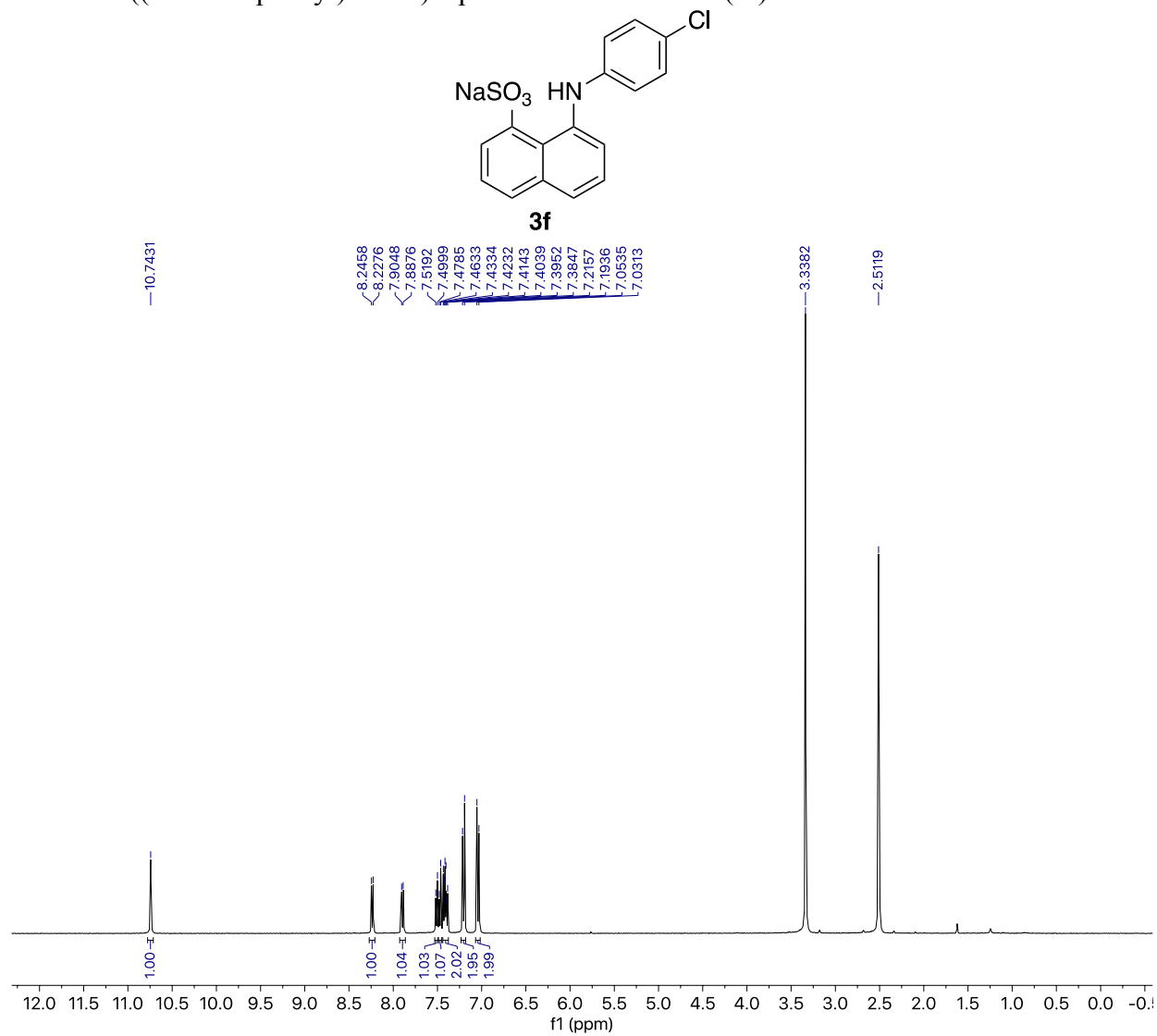
**Figure S17.** Carbon NMR for **3e**.



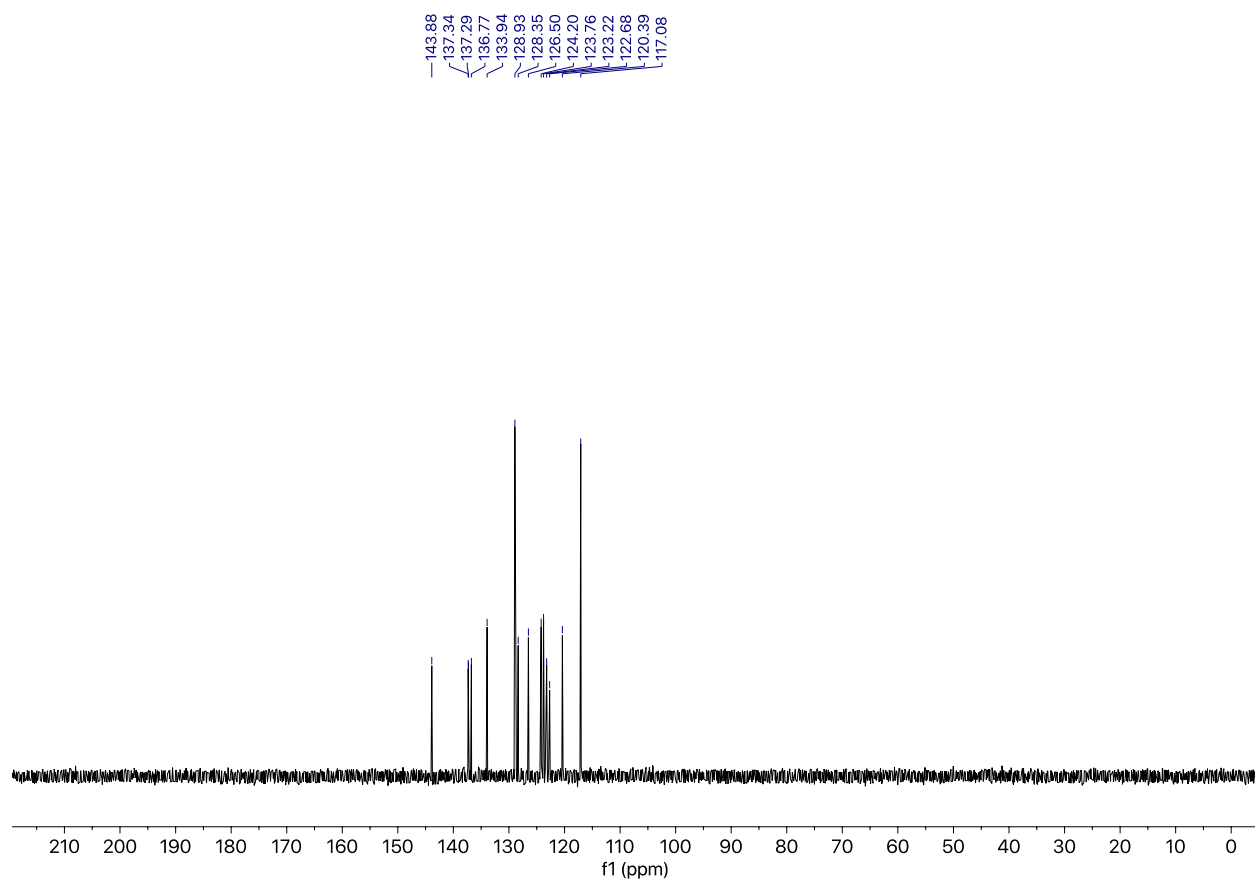
\*Fluorescence spectrum in ethylene glycol was taken at a lower gain to achieve an emission spectrum within the measurement parameters of the instrument.

**Figure S18.** Fluorescent spectra for **3e**.

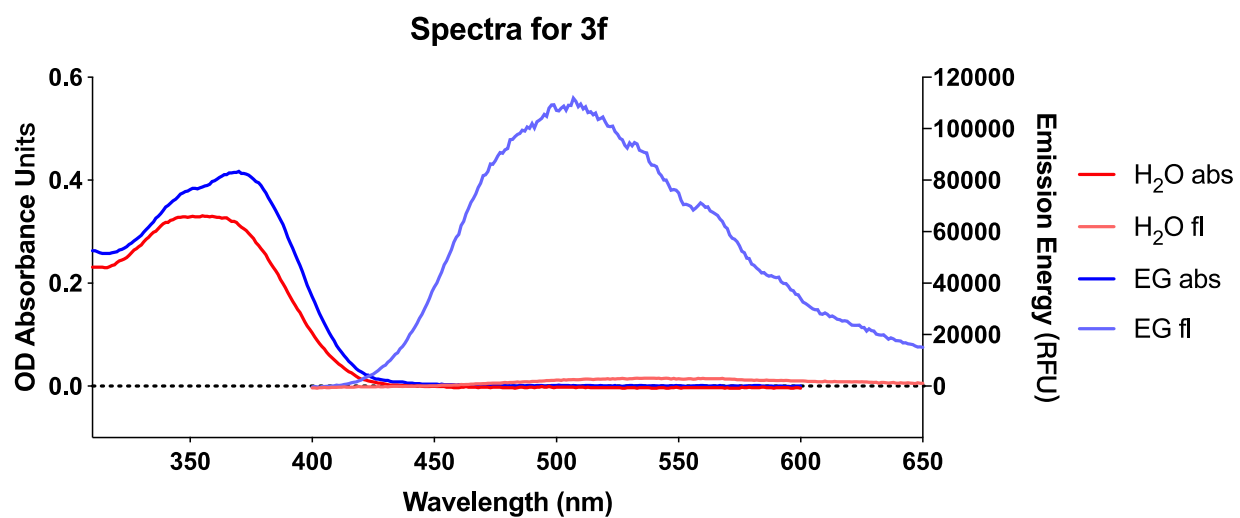
Sodium 8-((4-Chlorophenyl)amino)naphthalene-1-sulfonate (**3f**)



**Figure S19.** Proton NMR for **3f**.

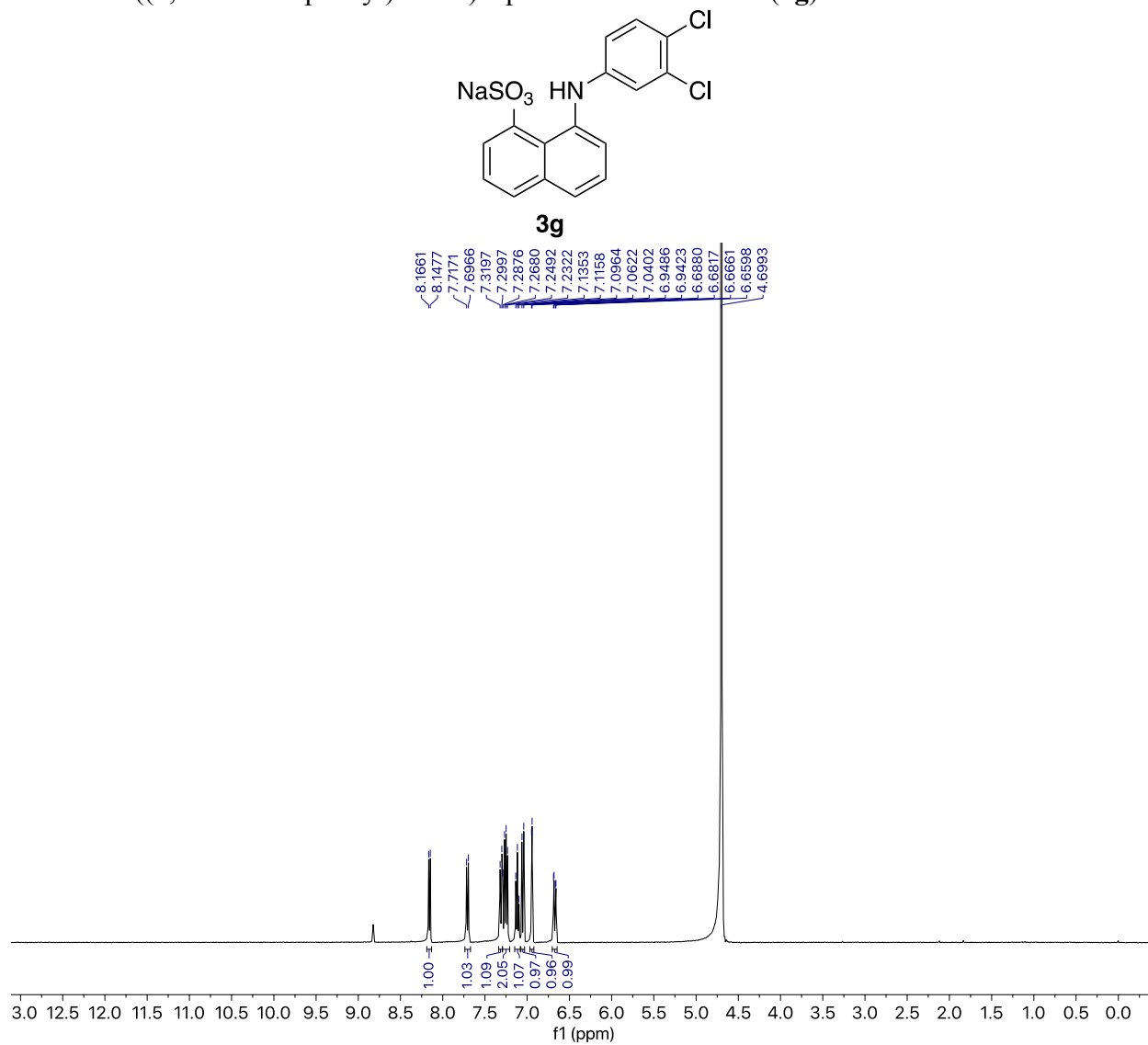


**Figure S20.** Carbon NMR for **3f**.

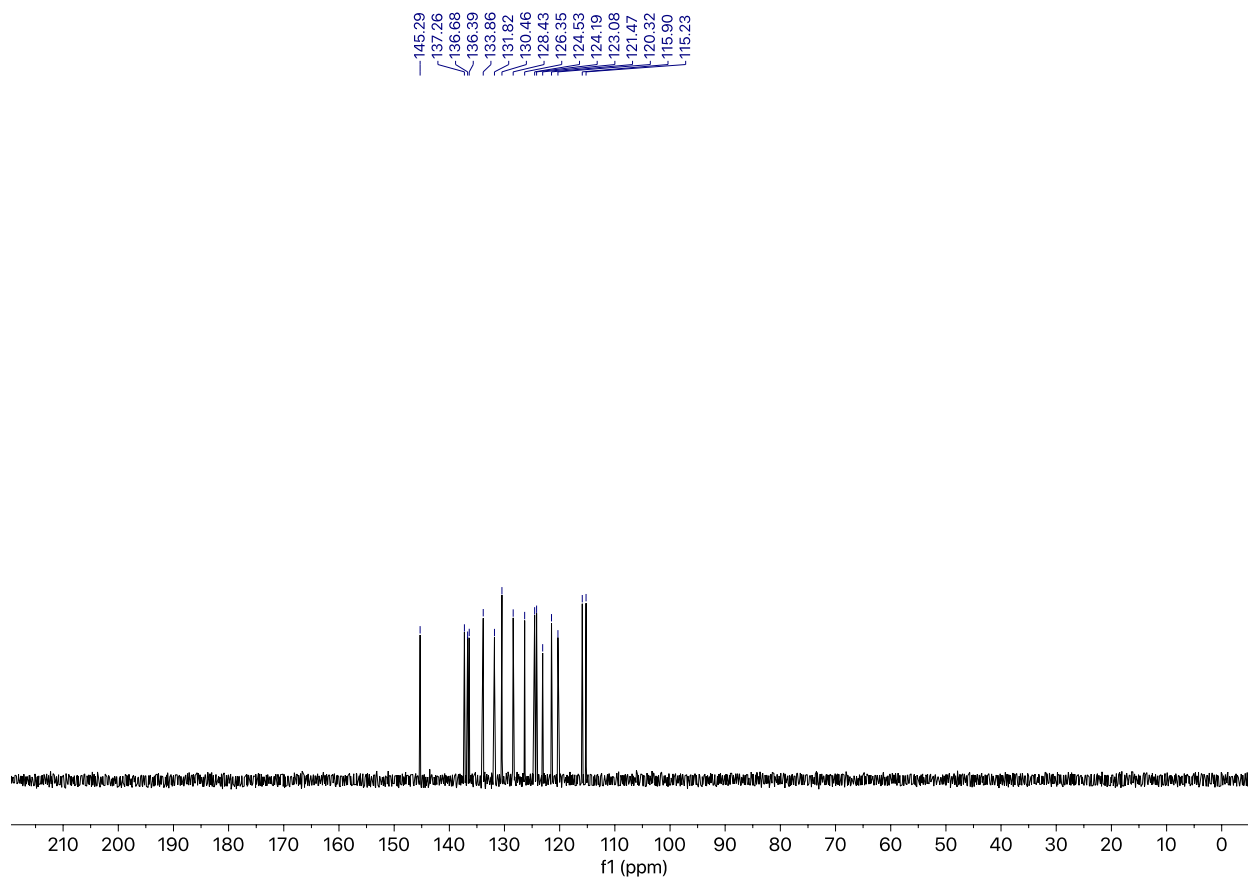


**Figure S21.** Fluorescent spectra for **3f**.

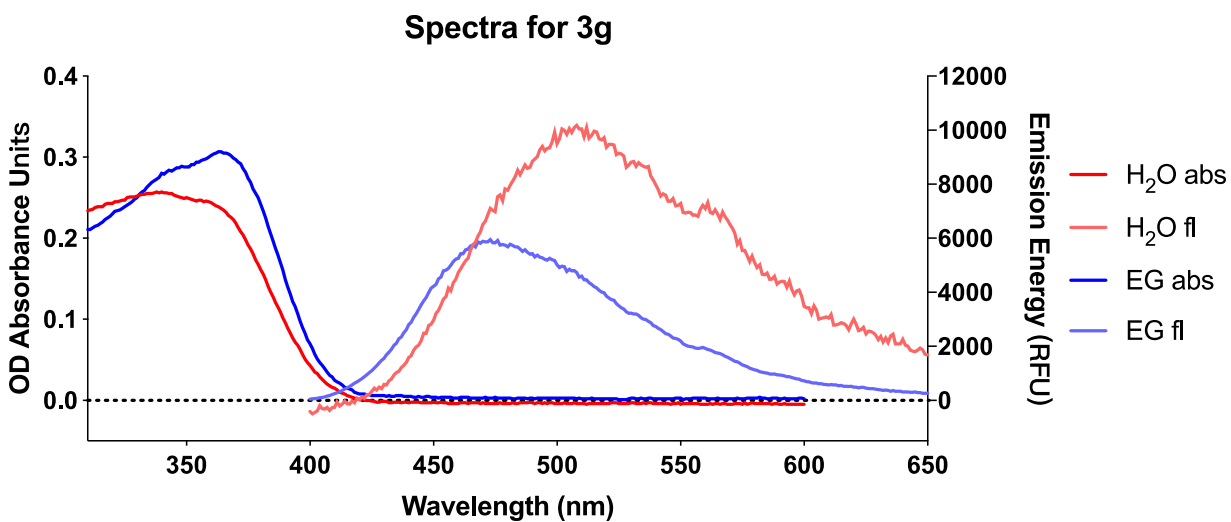
Sodium 8-((3,4-Dichlorophenyl)amino)naphthalene-1-sulfonate (**3g**)



**Figure S22.** Proton NMR for **3g**.



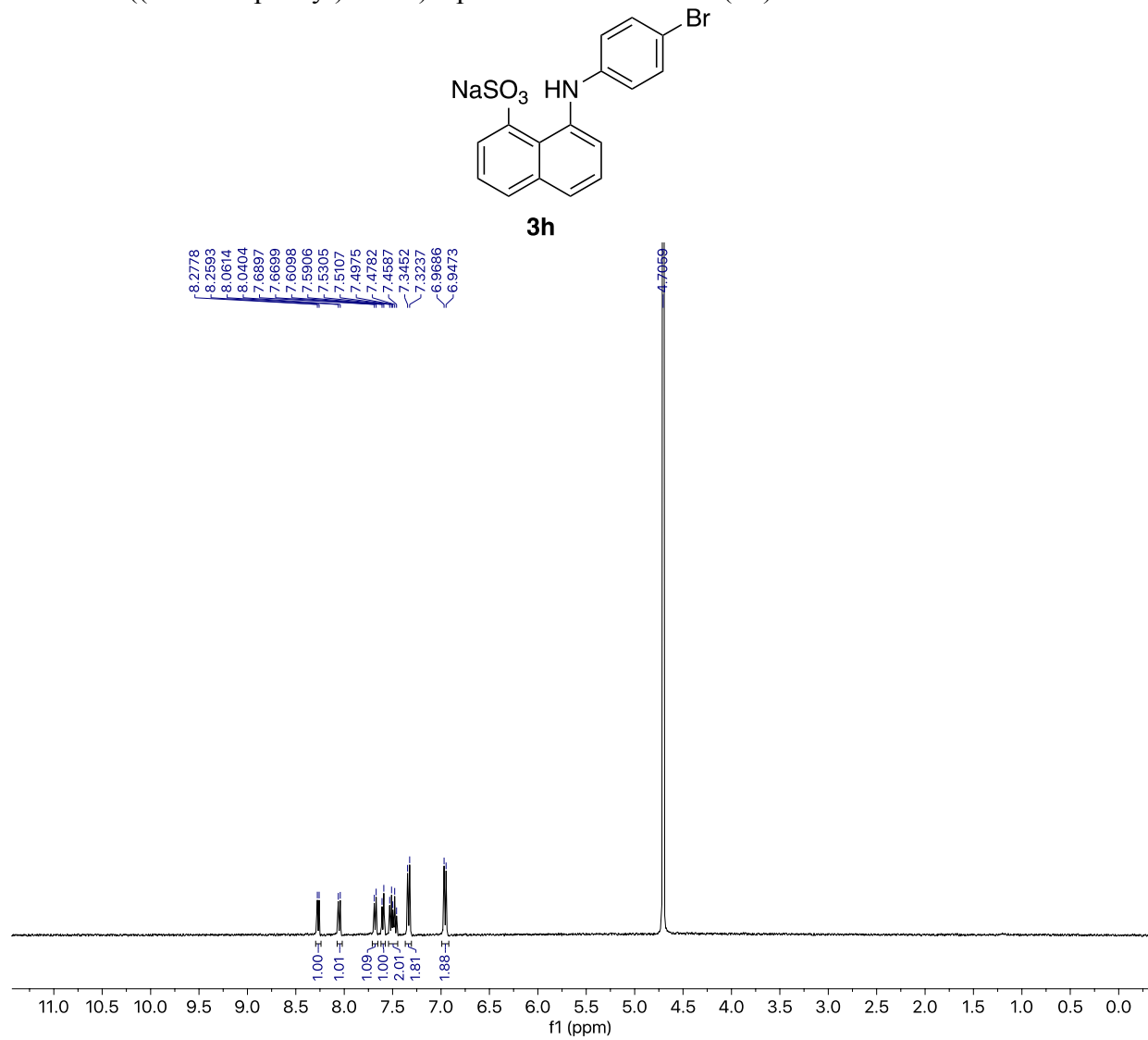
**Figure S23.** Carbon NMR for **3g**.



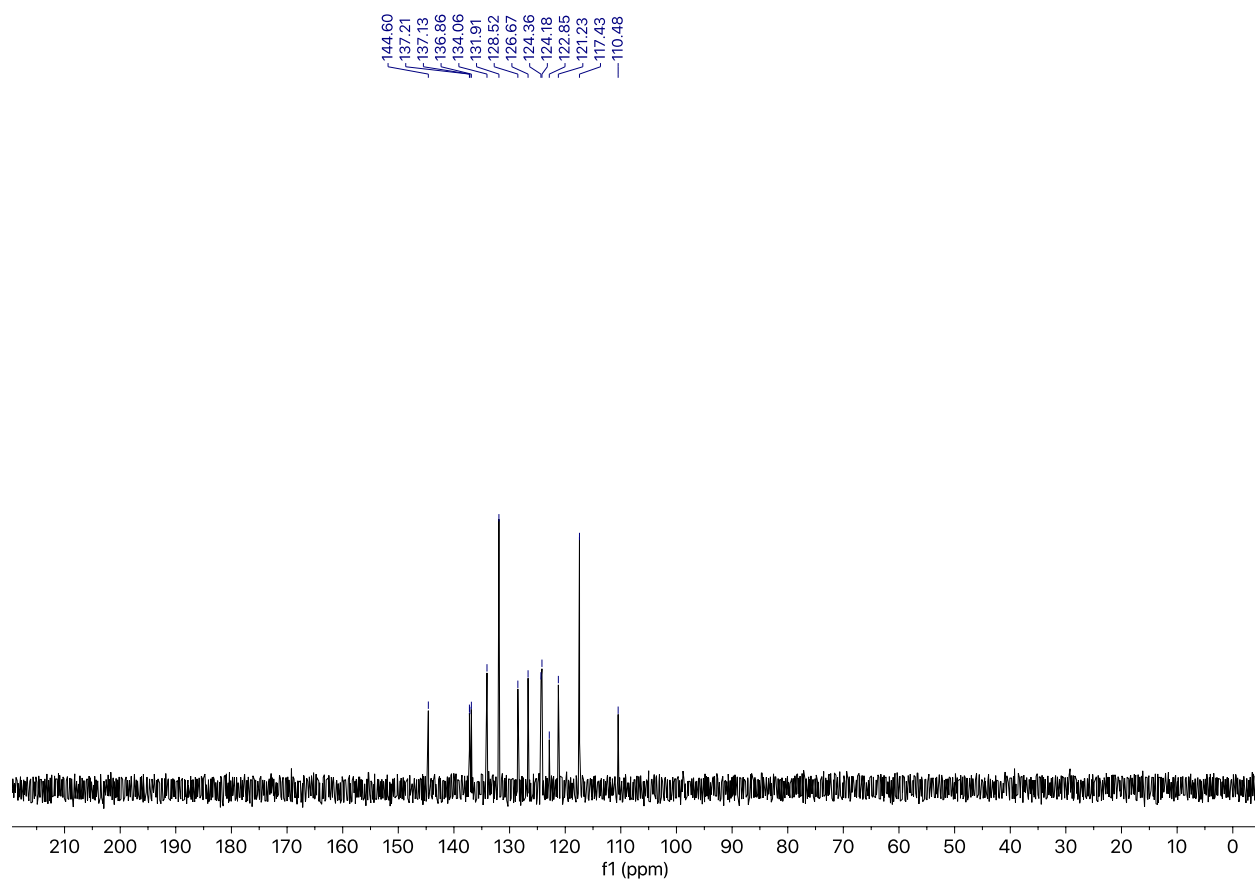
\*Fluorescence spectrum in ethylene glycol was taken at a lower gain to achieve an emission spectrum within the measurement parameters of the instrument.

**Figure S24.** Fluorescent spectra for **3g**.

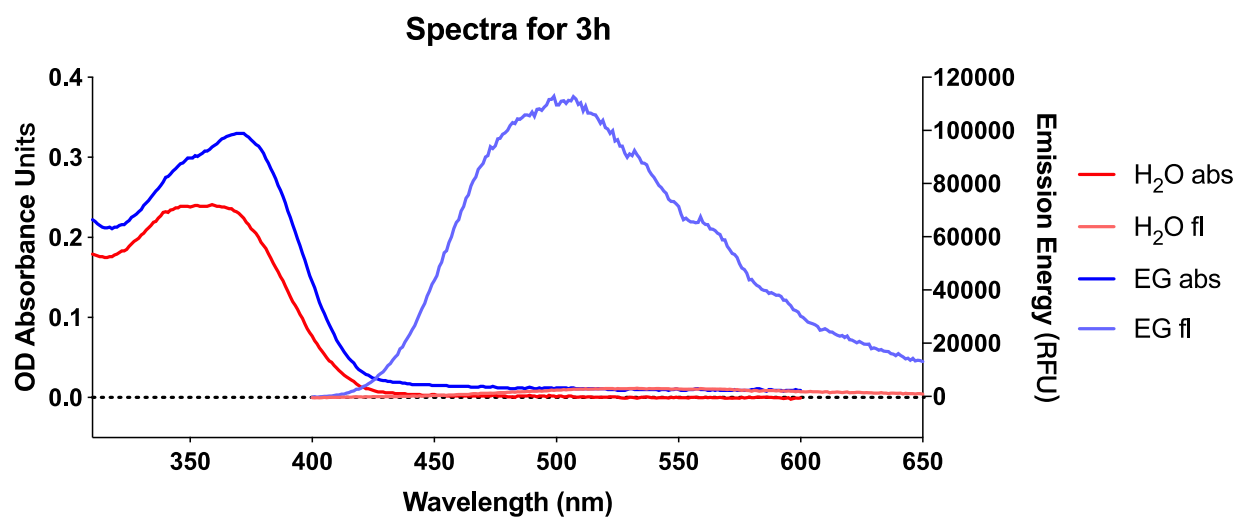
Sodium 8-((4-Bromophenyl)amino)naphthalene-1-sulfonate (**3h**)



**Figure S25.** Proton NMR for **3h**.



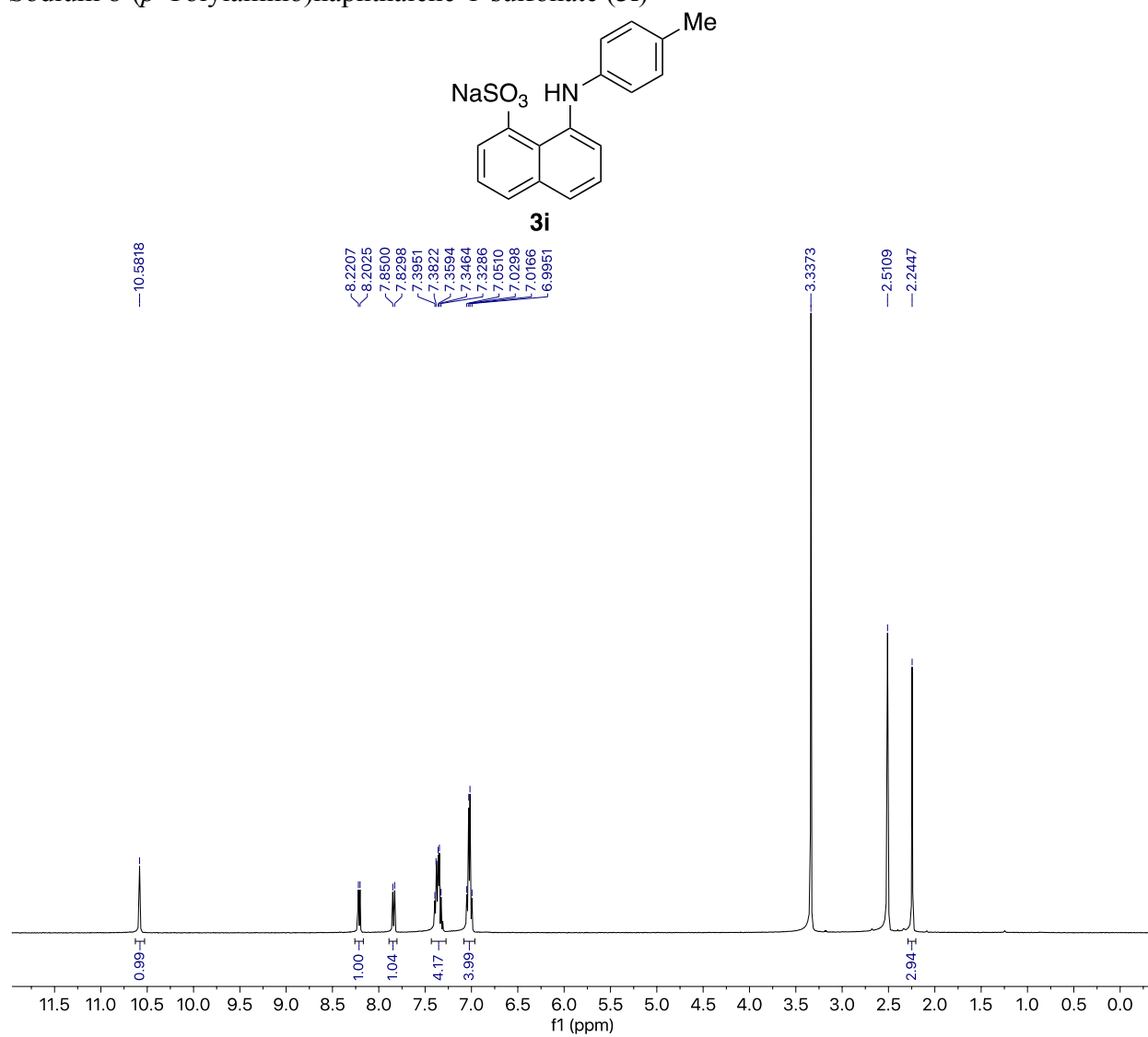
**Figure S26.** Carbon NMR for **3h**.



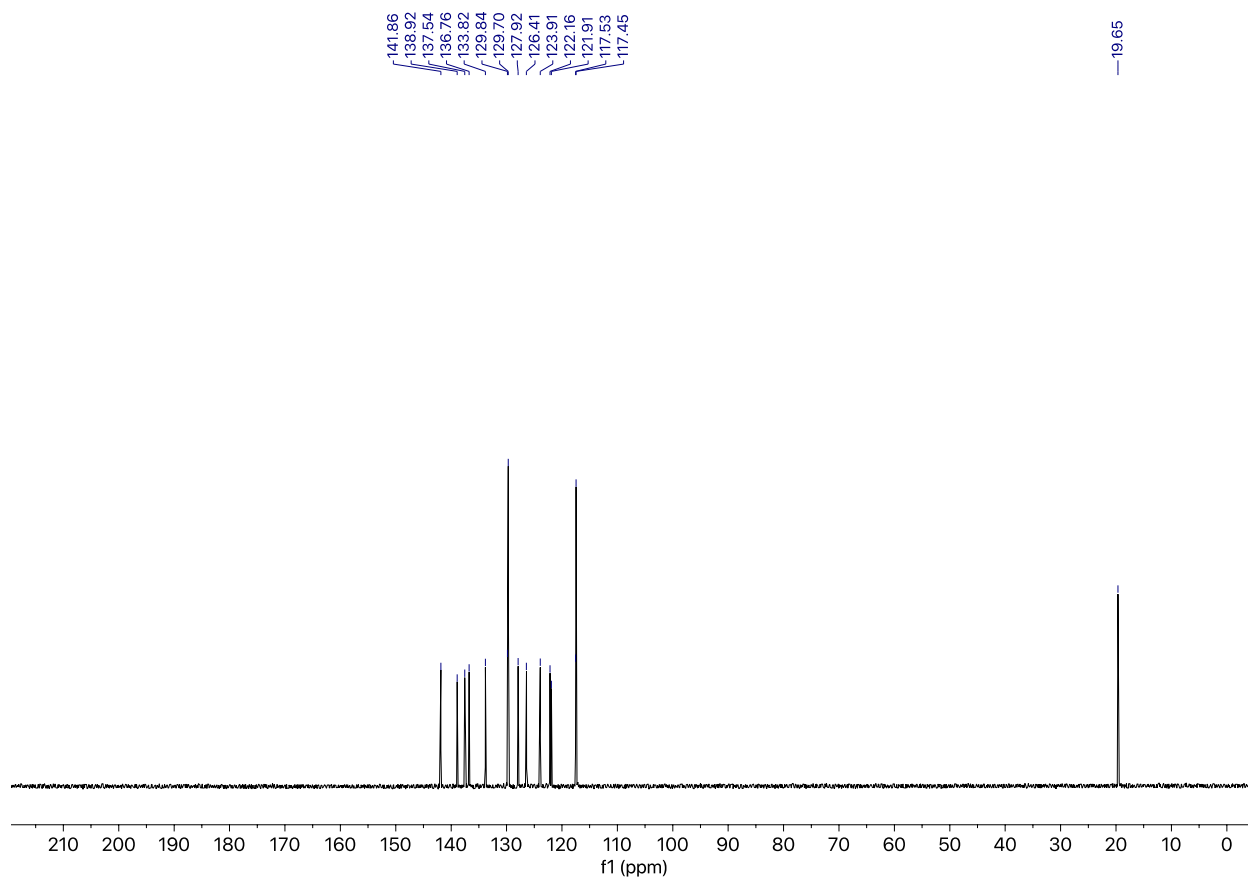
**Figure S27.** Fluorescent spectra for **3h**.



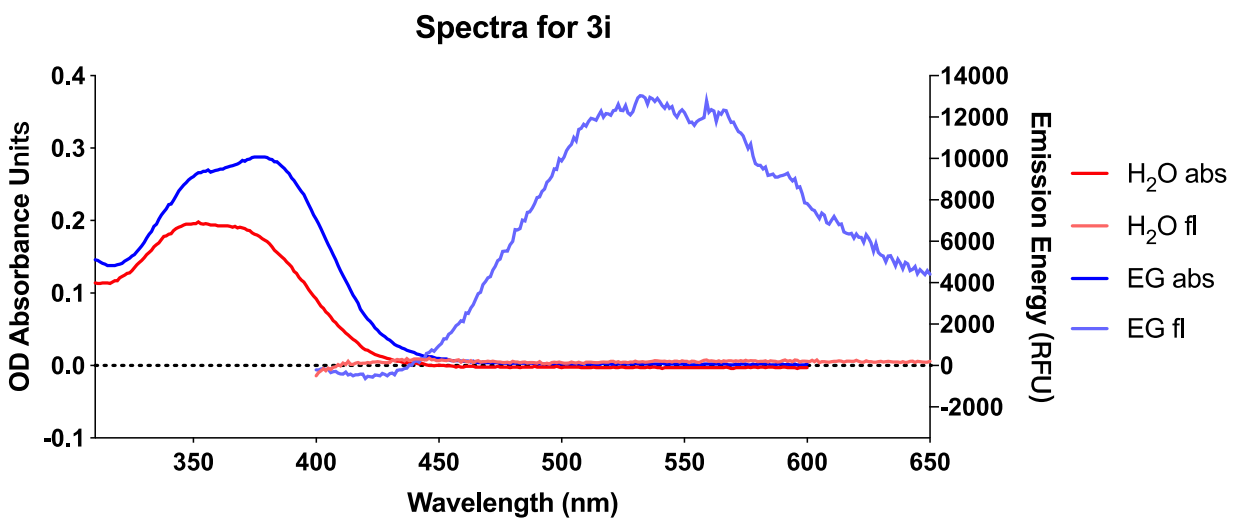
Sodium 8-(*p*-Tolylamino)naphthalene-1-sulfonate (**3i**)



**Figure S28.** Proton NMR for **3i**.

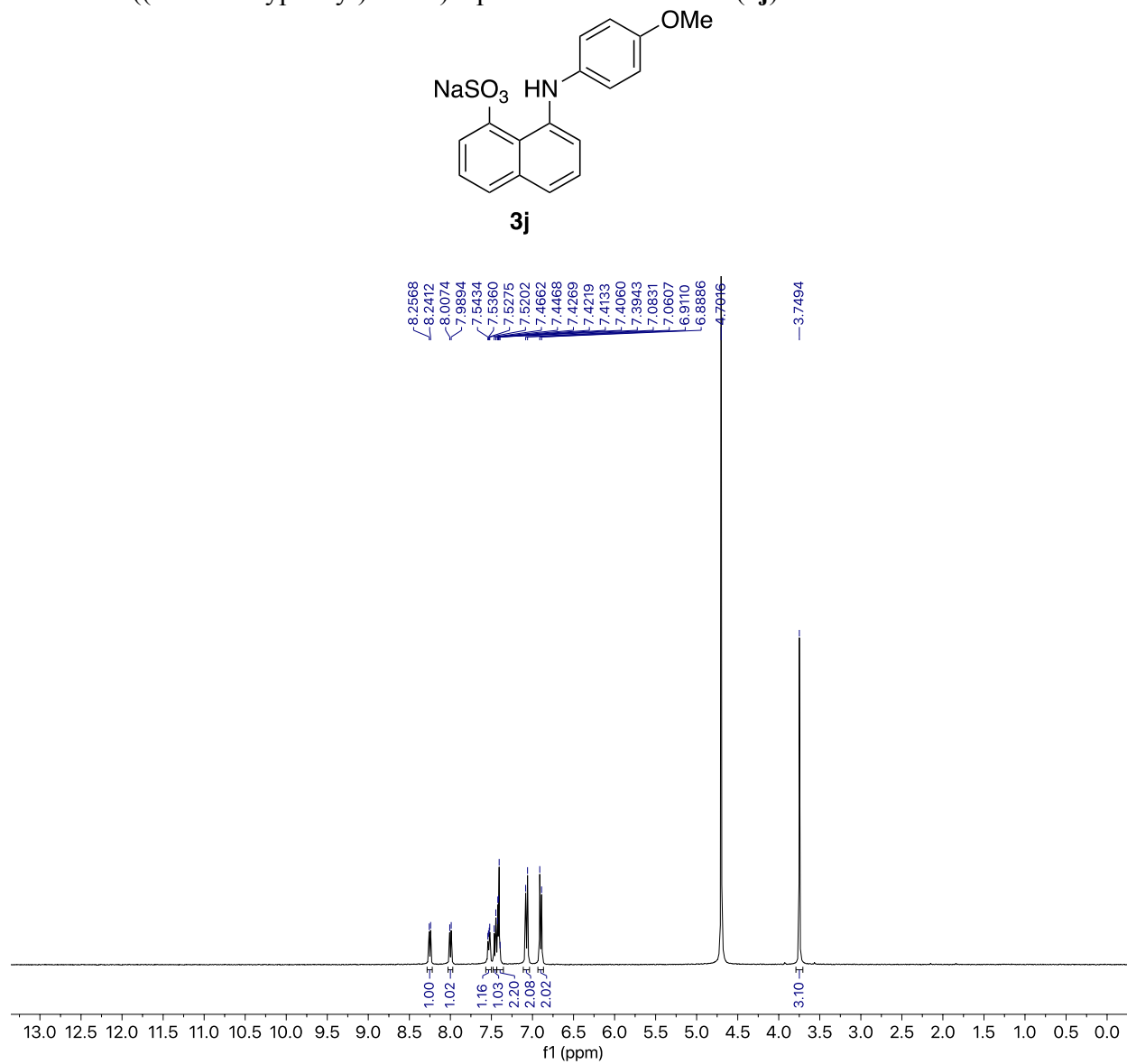


**Figure S29.** Carbon NMR for **3i**.



**Figure S30.** Fluorescent spectra for **3i**.

Sodium 8-((4-Methoxyphenyl)amino)naphthalene-1-sulfonate (**3j**)



**Figure S31.** Proton NMR for **3j**.

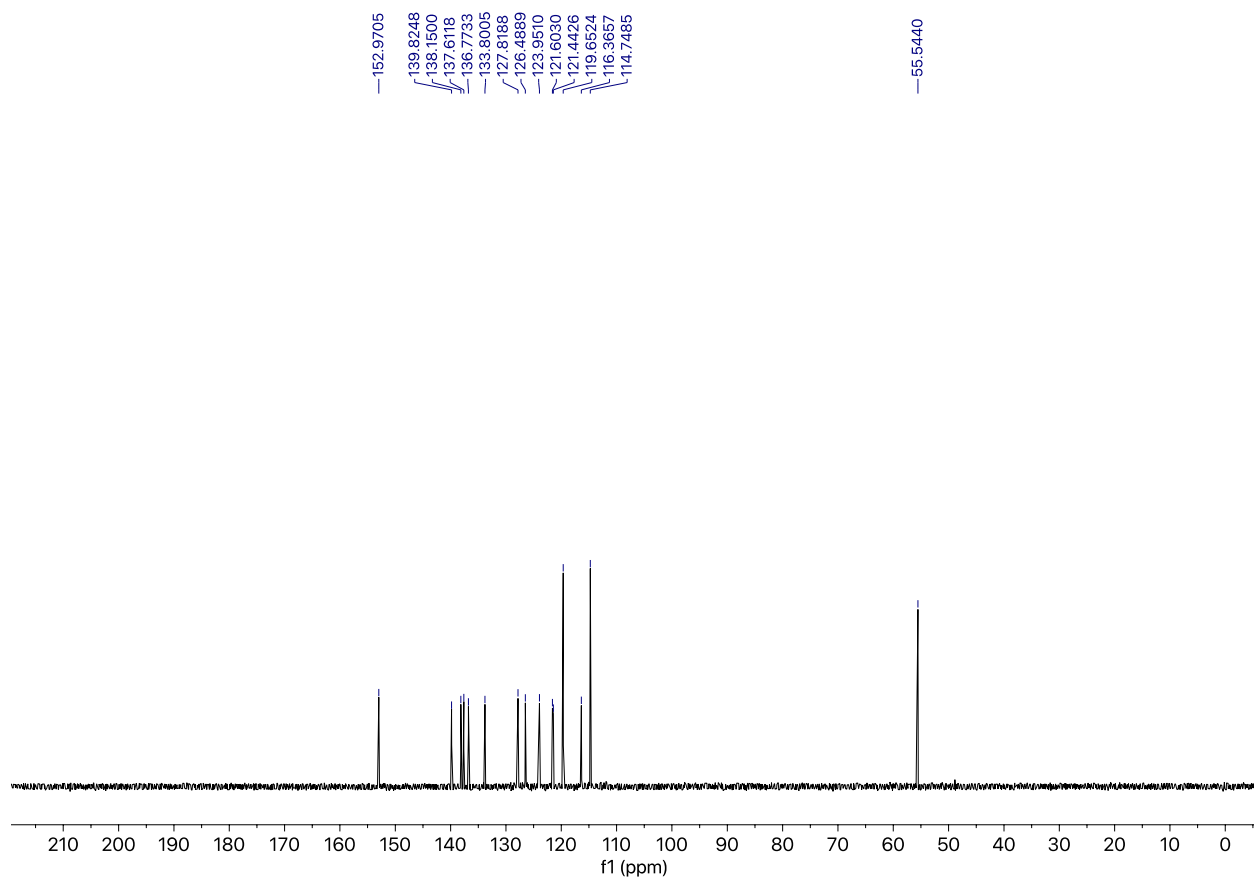


Figure S32. Carbon NMR for **3j**.

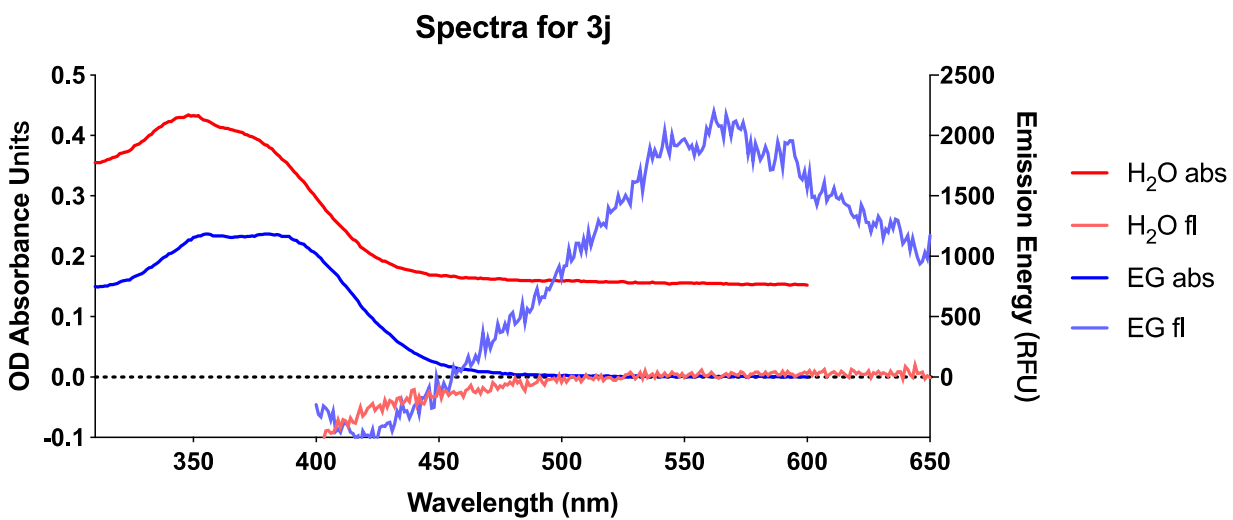
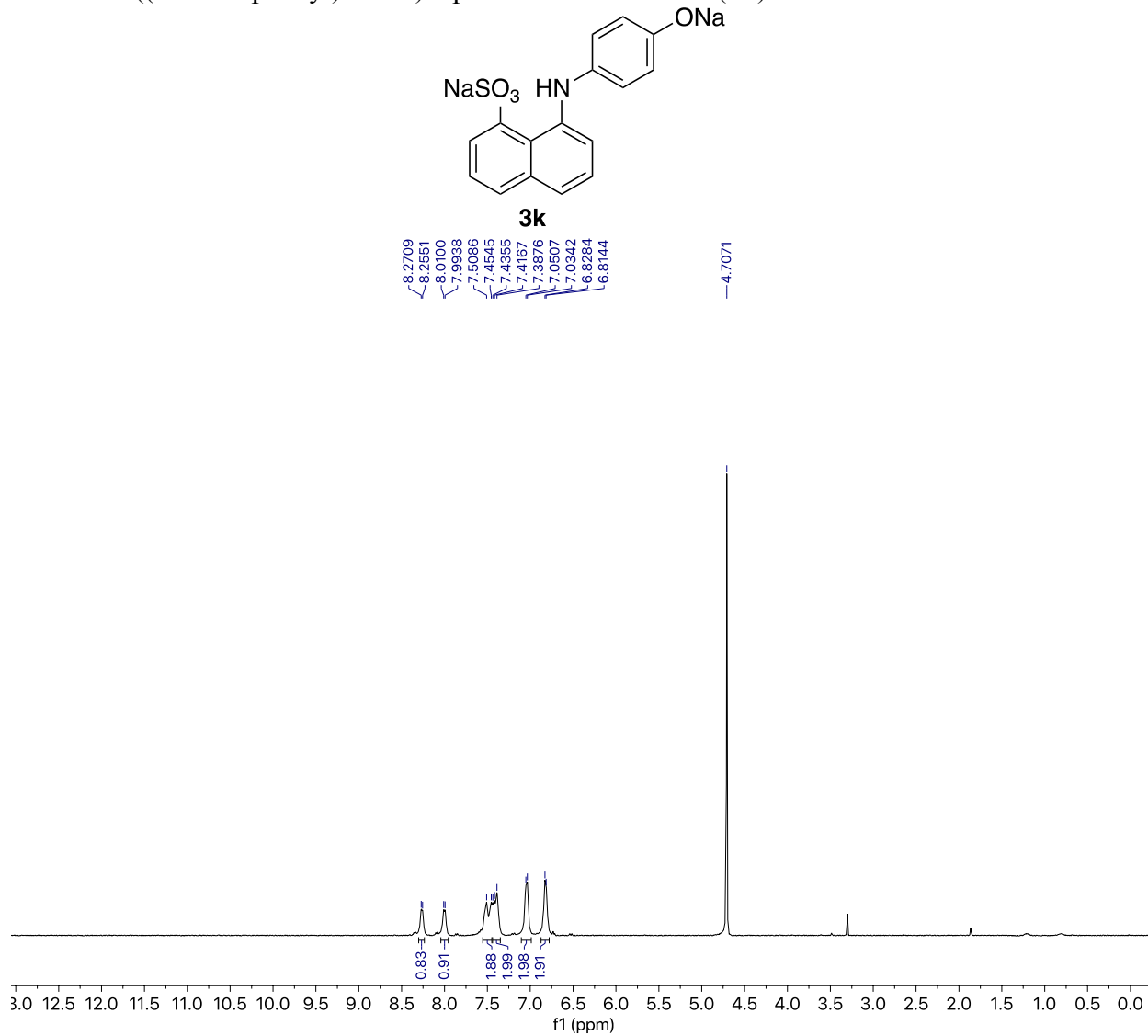
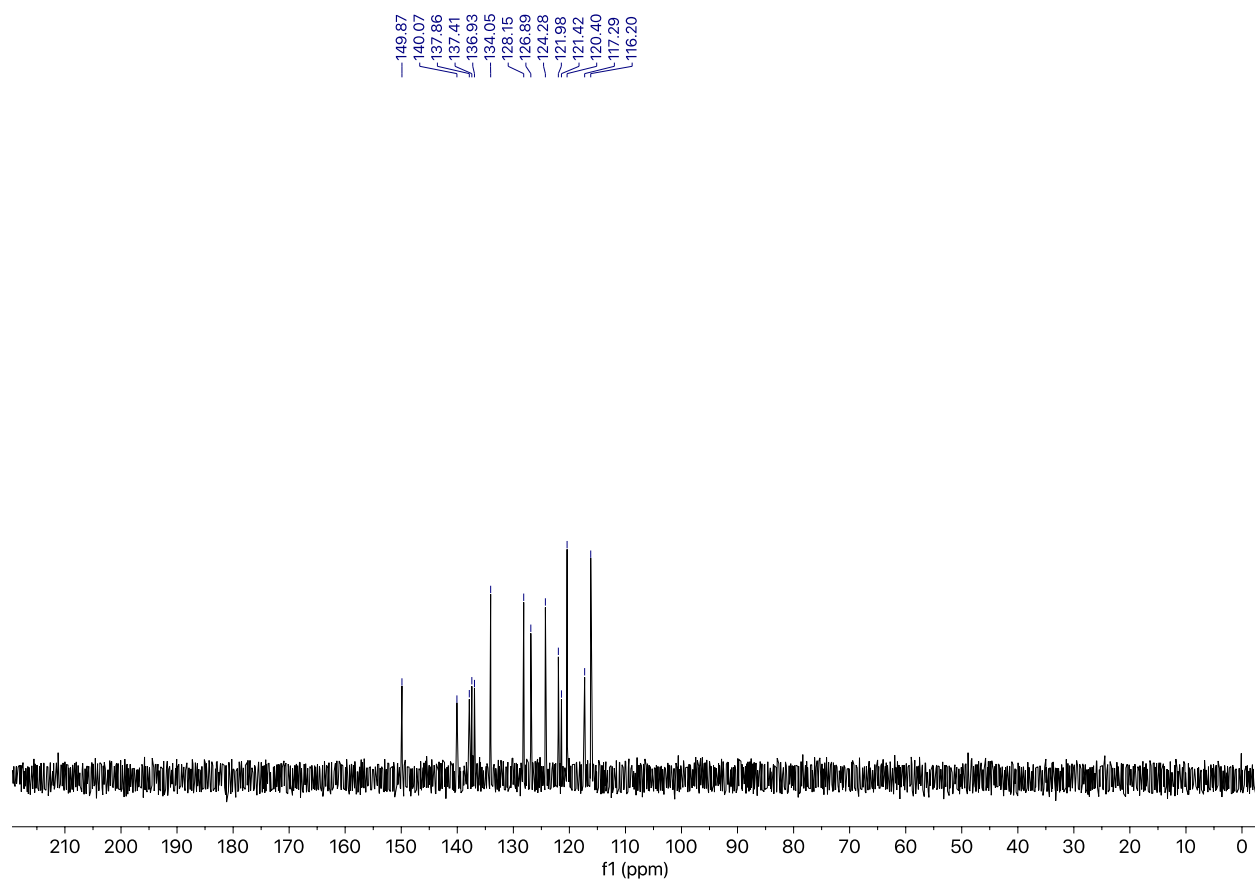


Figure S33. Fluorescent spectra for **3j**.

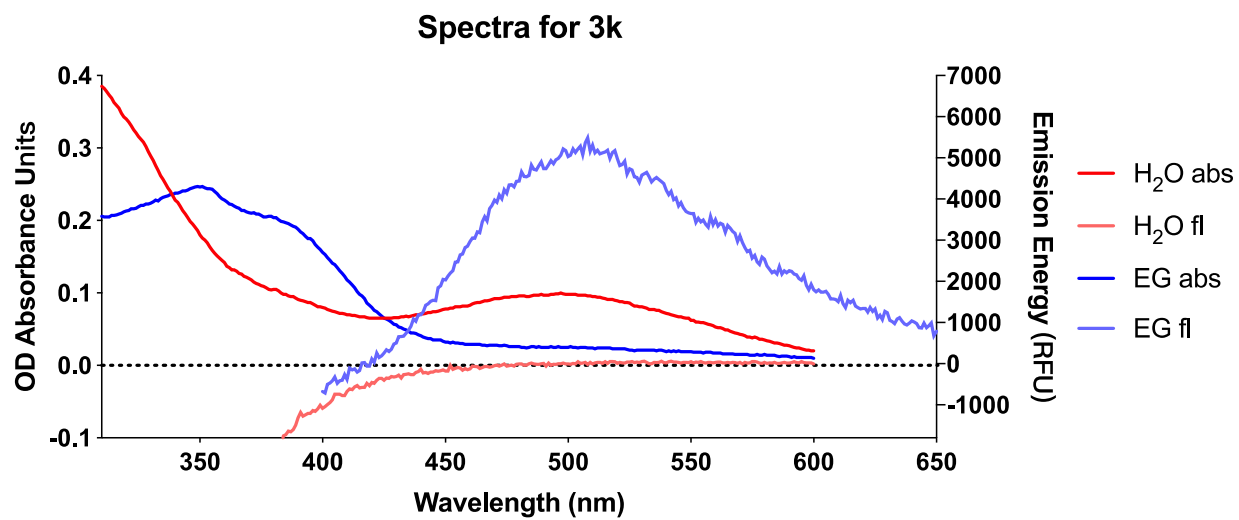
Sodium 8-((4-Oxidophenyl)amino)naphthalene-1-sulfonate (**3k**)



**Figure S34.** Proton NMR for **3k**.

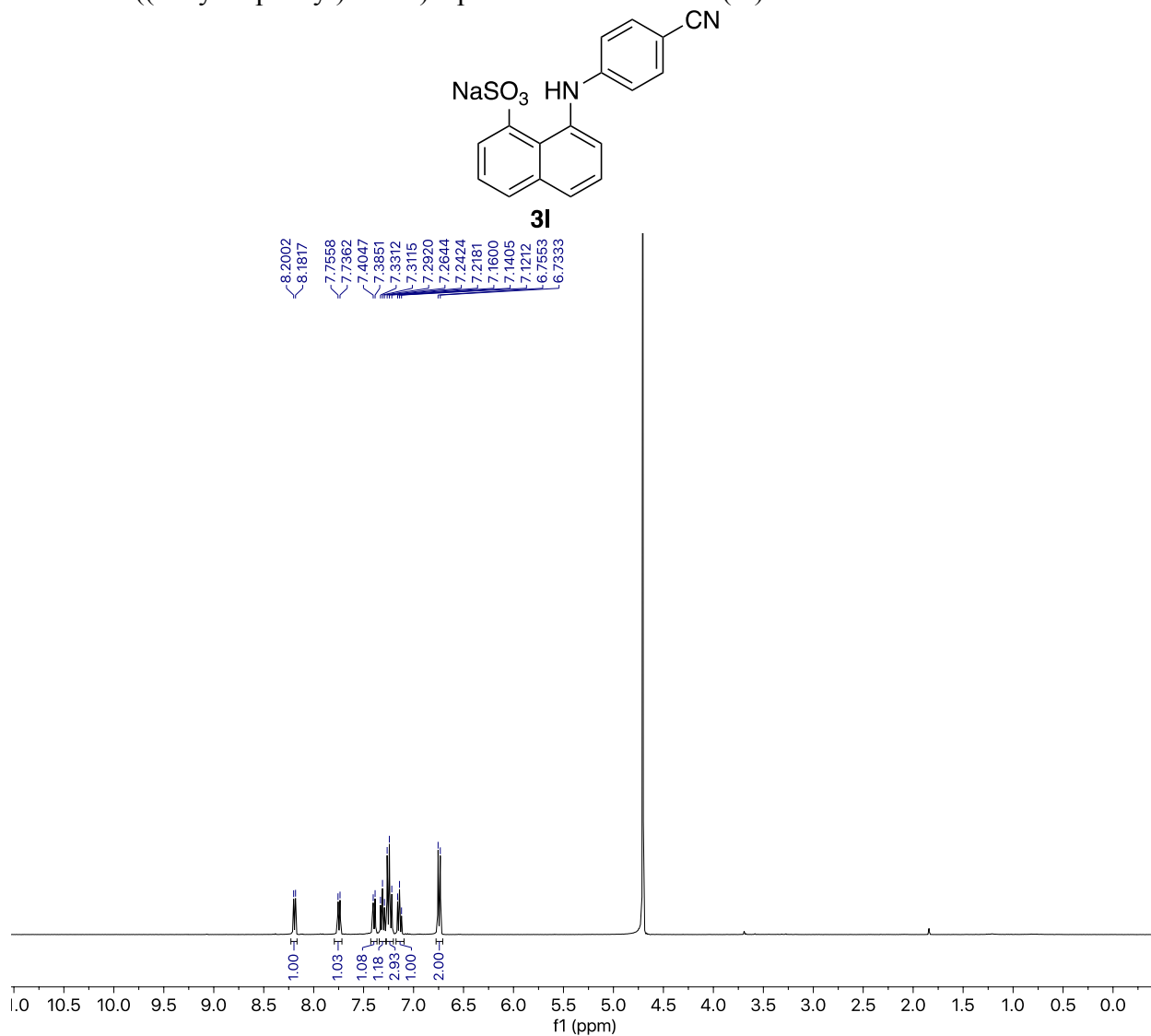


**Figure S35.** Carbon NMR for **3k**.



**Figure S36.** Fluorescent spectra for **3k**.

Sodium 8-((4-Cyanophenyl)amino)naphthalene-1-sulfonate (**3I**)



**Figure S37.** Proton NMR for **3I**.

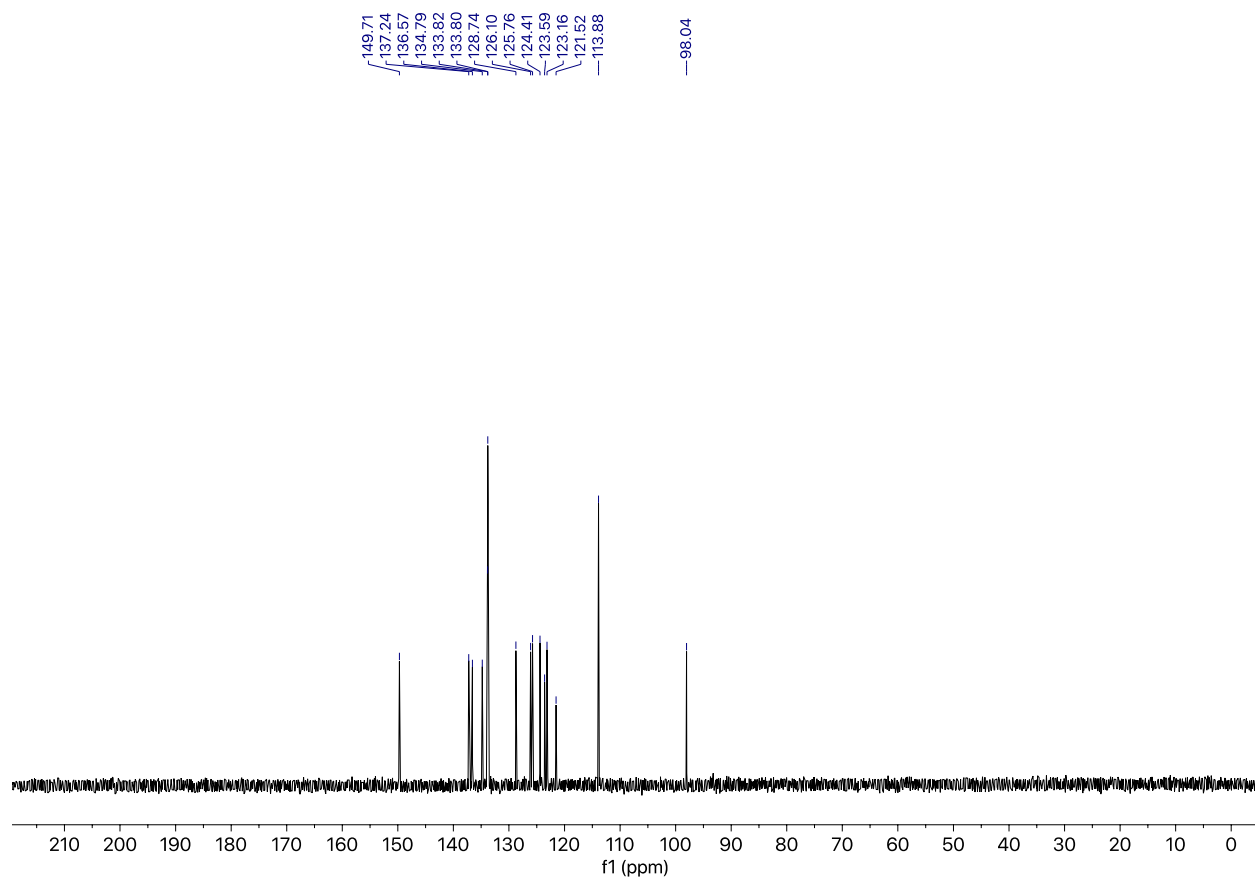


Figure S38. Carbon NMR for **31**.

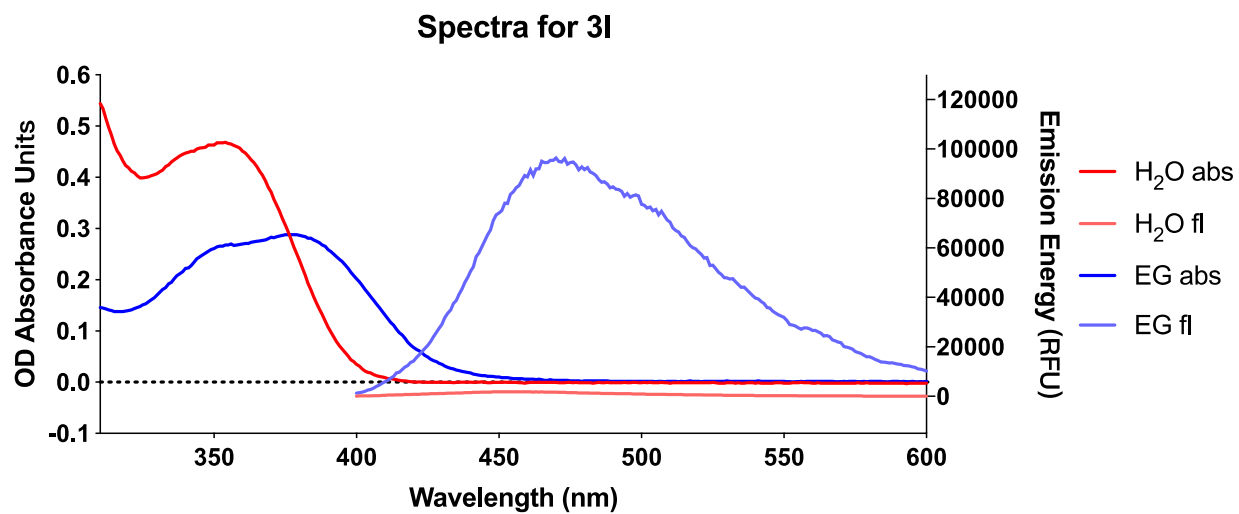
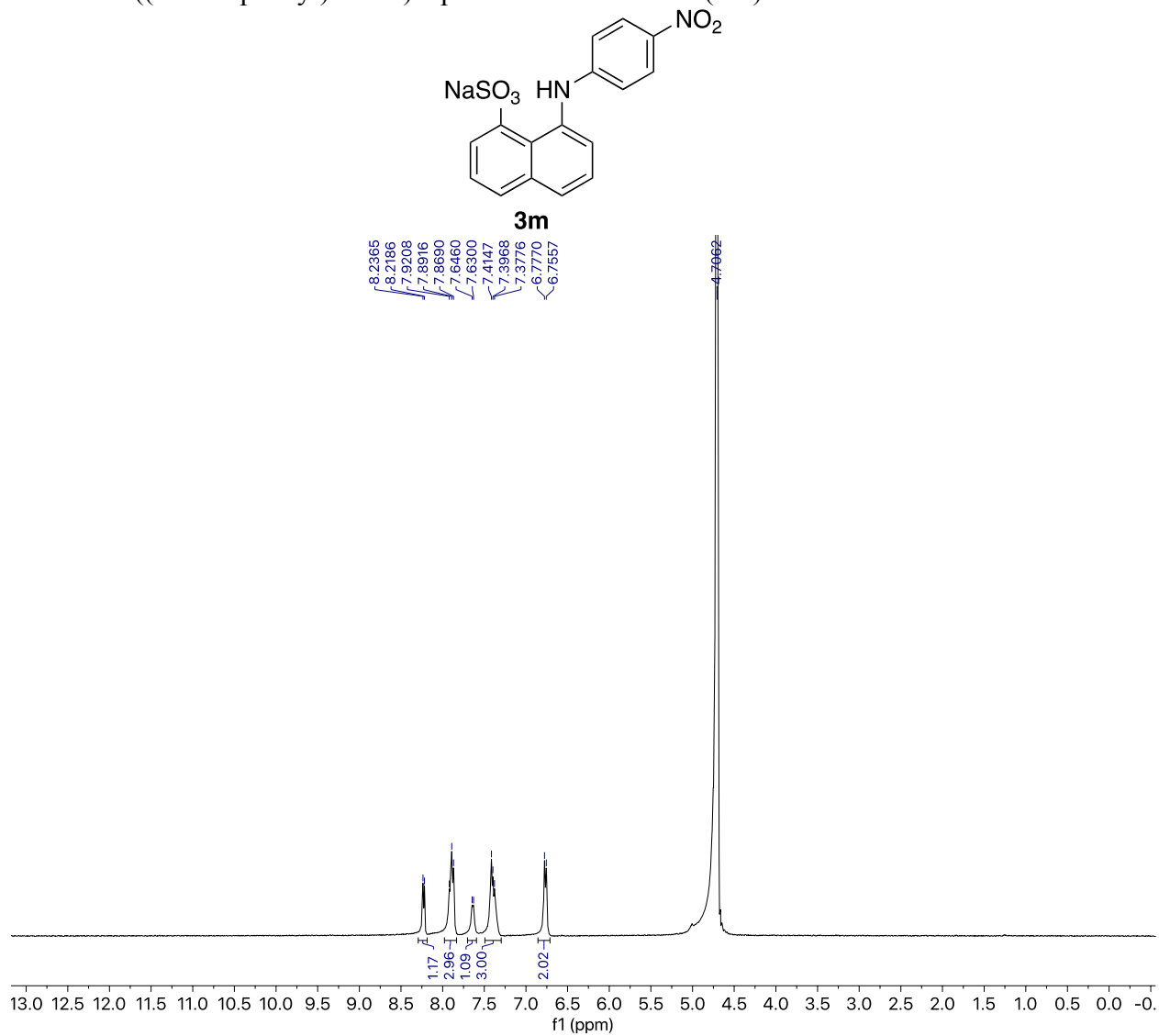


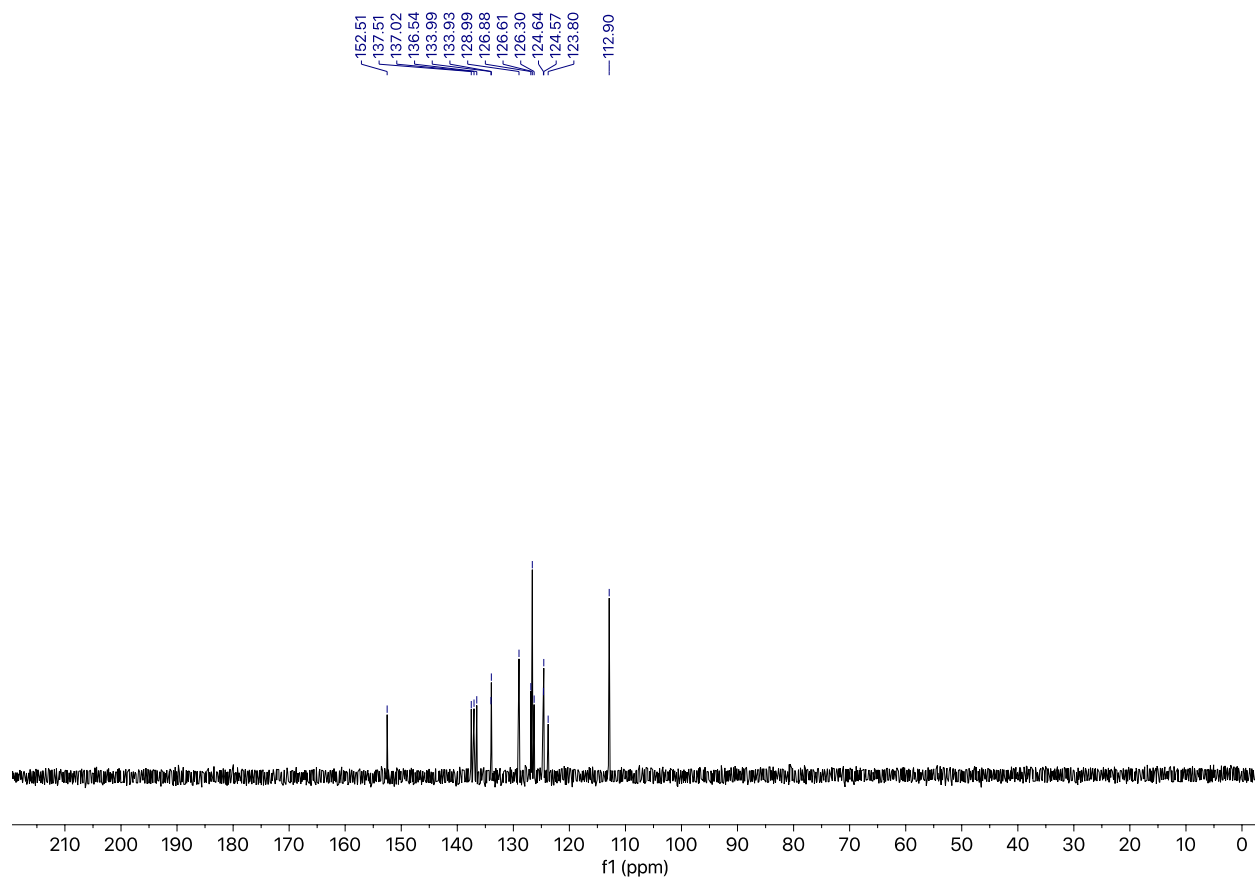
Figure S39. Fluorescent spectra for **31**.



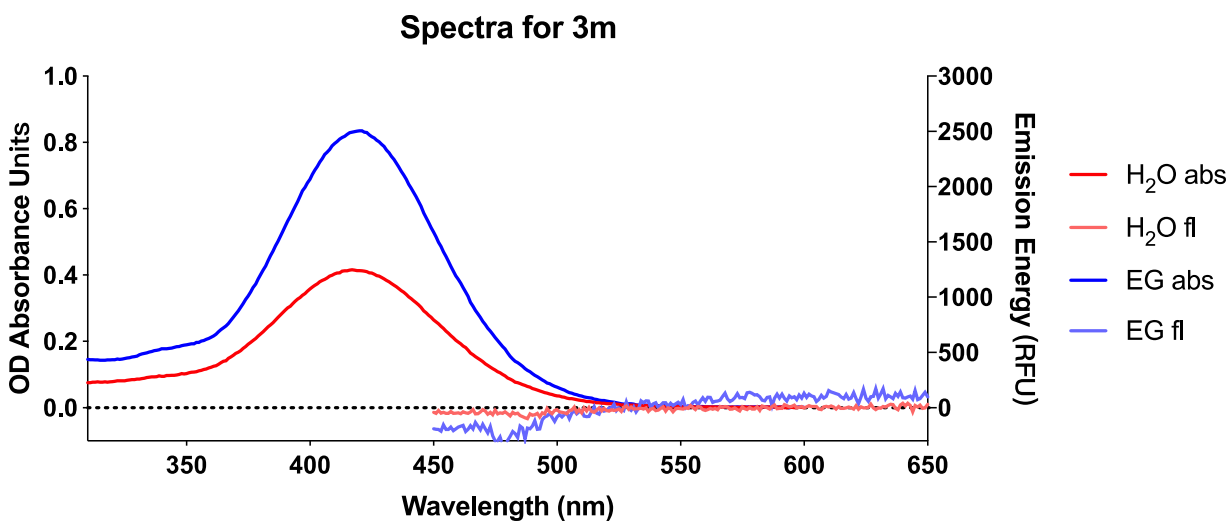
Sodium 8-((4-Nitrophenyl)amino)naphthalene-1-sulfonate (**3m**)



**Figure S40.** Proton NMR for **3m**.

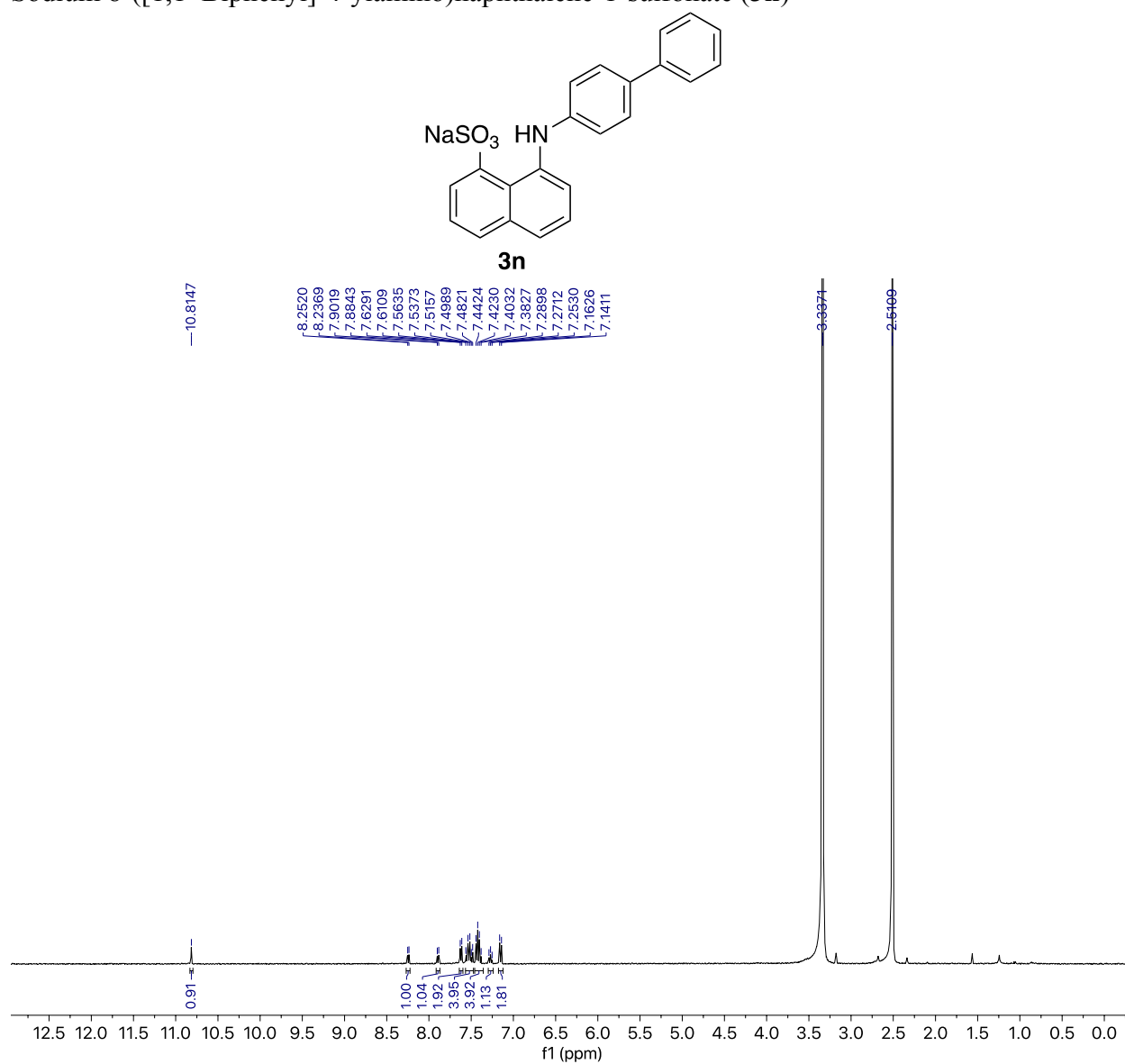


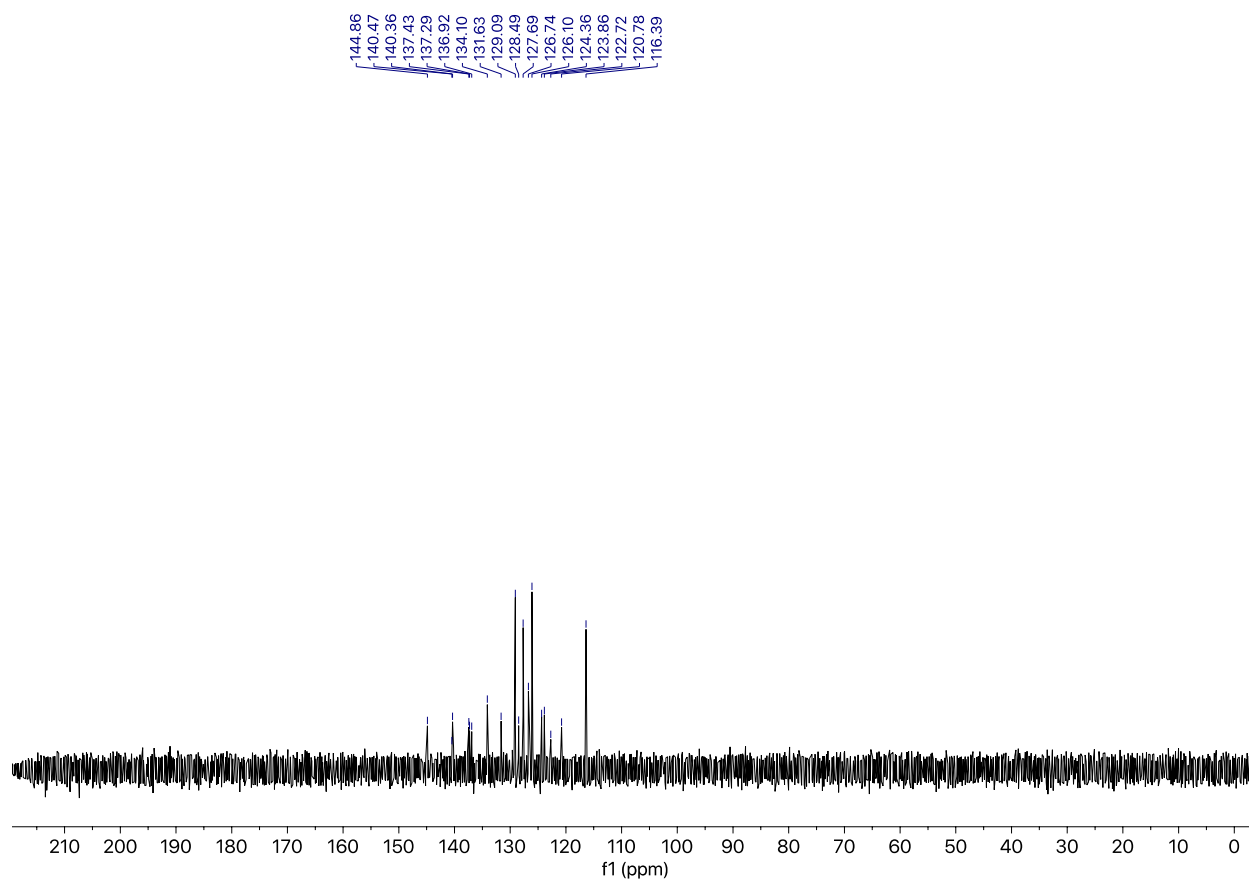
**Figure S41.** Carbon NMR for **3m**.



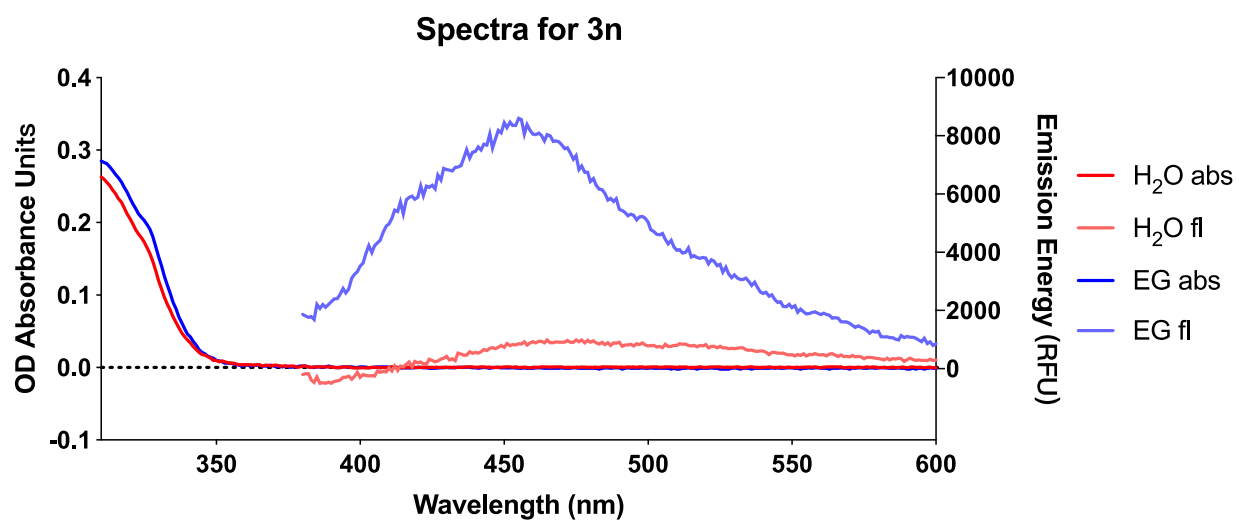
**Figure S42.** Fluorescent spectra for **3m**.

Sodium 8-([1,1'-Biphenyl]-4-ylamino)naphthalene-1-sulfonate (**3n**)



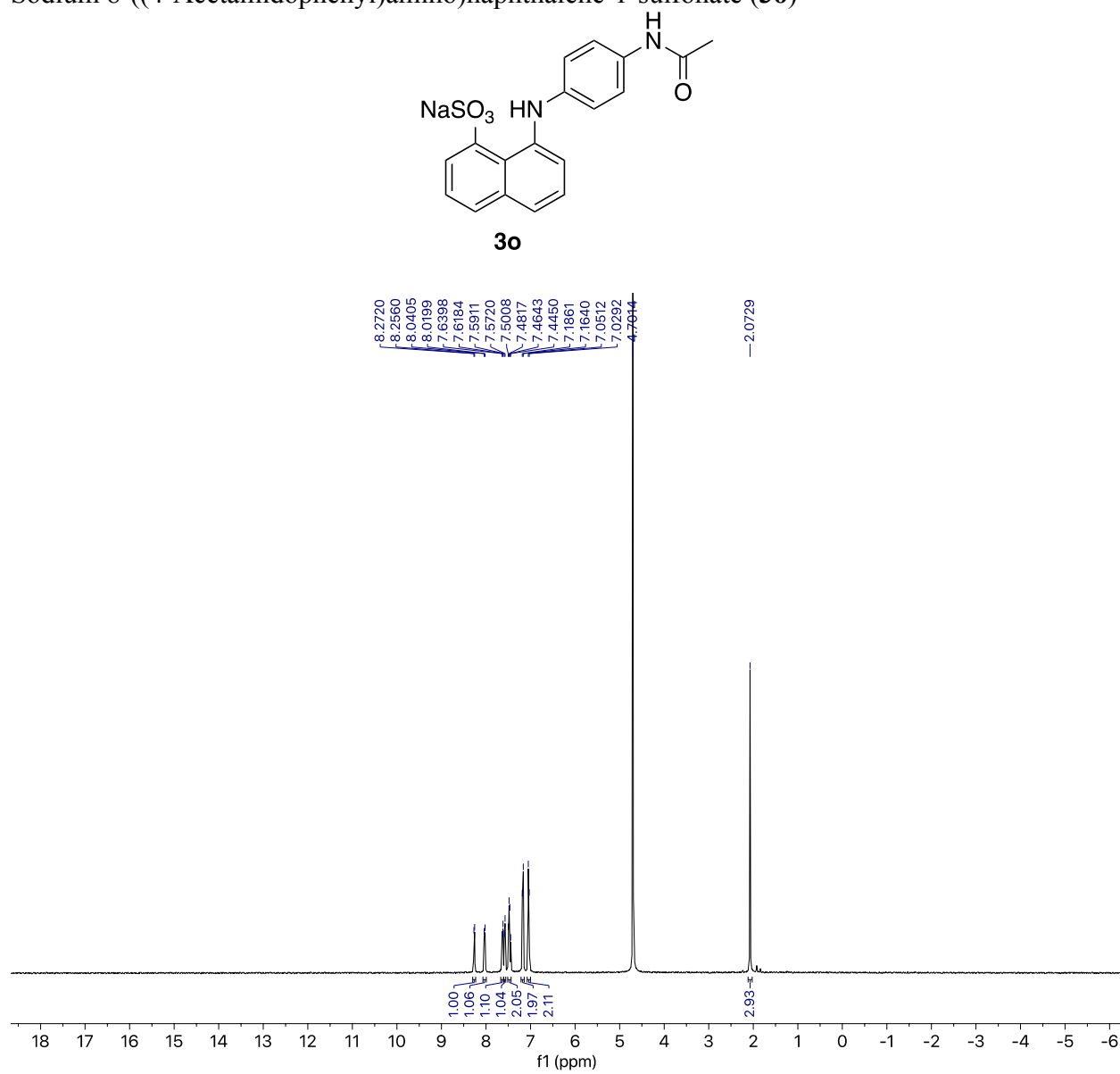


**Figure S44.** Carbon NMR for **3n**.

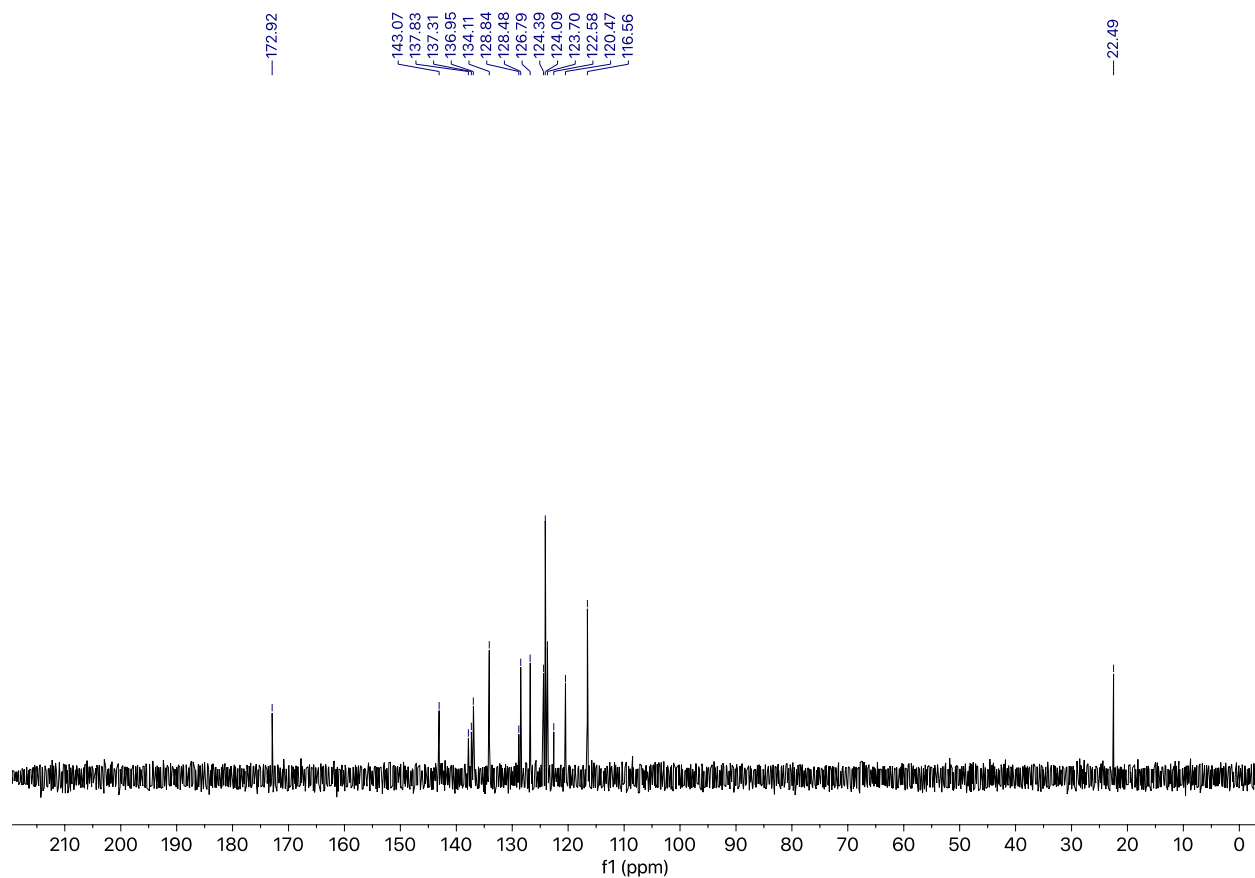


**Figure S45.** Fluorescent spectra for **3n**.

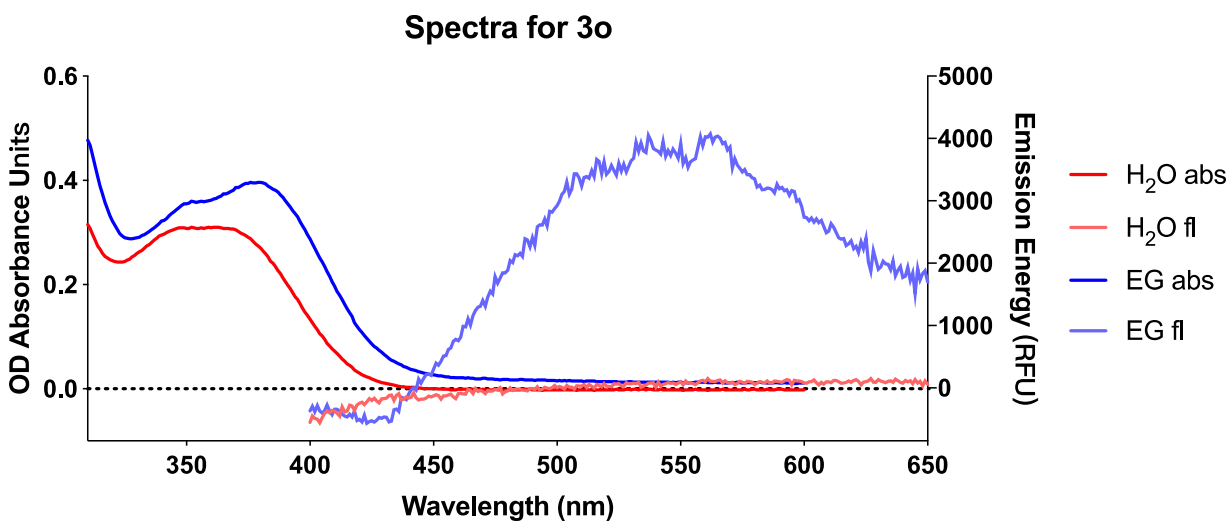
Sodium 8-((4-Acetamidophenyl)amino)naphthalene-1-sulfonate (**3o**)



**Figure S46.** Proton NMR for **3o**.



**Figure S47.** Carbon NMR for **3o**.



**Figure S48.** Fluorescent spectra for **3o**.

### III. Hammett Plot of ANS derivatives

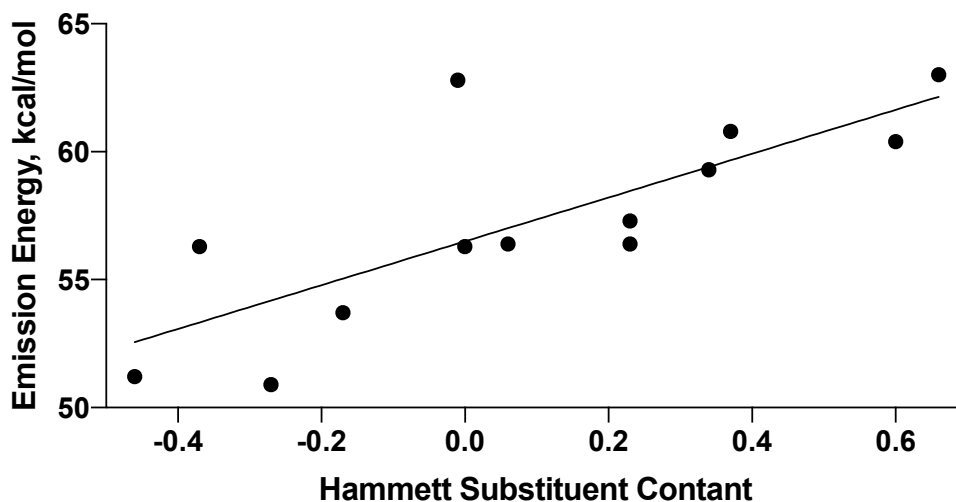


Figure S49. Hammett Plot for ANS derivatives.

### IV. References

1. Baqi, Y.; Muller, C. E. Rapid and efficient microwave-assisted copper(0)-catalyzed ullmann coupling reaction: general access to anilinoanthraquinone derivatives. *Org. Lett.* **2007**, *9*, 1271-1274.
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