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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IV. References
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:** To 8-chloronaphthalene-1-sulfonic acid (1, 1 equiv), elemental copper (cat. amount), and aniline (2a, 2 equiv) in H₂O, were added NaH₂PO₄ and Na₂HPO₄ to adjust the pH to 6-7. Then the reaction was conducted under microwave conditions at 90 °C for 20 min.

**Method B:** To 1 (1 equiv) in DMF, were added tetramethylethylenediamine (TMEDA, cat. amount), CuI (cat. amount), K₂CO₃ (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 Na₂HPO₄ (pH 9.6) and NaH₂PO₄ (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

| 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.

Figure S3. Fluorescent spectra 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.
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.

*S 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.
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 3l.

Figure S39. Fluorescent spectra for 3l.
Sodium 8-((4-Nitrophenyl)amino)naphthalene-1-sulfonate (3m)

Figure S40. Proton NMR for 3m.
**Figure S41.** Carbon NMR for 3m.

![Carbon NMR spectrum for 3m](image)

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

![Fluorescent spectra for 3m](image)
Sodium 8-([1,1'-Biphenyl]-4-ylamino)naphthalene-1-sulfonate (3n)

Figure S43. Proton NMR for 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

![Hammett Plot for ANS derivatives](image)

**Figure S49.** Hammett Plot for ANS derivatives.

IV. References

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