Electronic Supporting Information for

Modifying a Known Gelator Scaffold for Nitrite Detection

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Contents:

I. Materials

All reagent grade materials and solvents were purchased from Sigma-Aldrich, Acros, or TCI. Anilines were distilled under vacuum before each use. Compounds **3a-g** were prepared from modified literature procedures.[1] Deionized water was used unless otherwise specified. Thermogravimetric analysis of the sodium 2-naphthol-6-sulfonate hydrate revealed 2.024 H_2O molecules on average. For the synthetic procedures, an average of 2 H_2O molecules was used.

II. General Experimental

NMR Spectroscopy – ^{1}H and ^{13}C NMR spectra for all compounds were acquired in d_6-DMSO or D_2O on a Varian vnmr 700 operating at 700 and 176 MHz, or a Varian Inova 500 operating at 500 and 126 MHz. The chemical shift data are reported in units of δ (ppm) relative to tetramethylsilane and referenced by residual protic solvent. An asterisk was used to indicate residual H_2O in all spectra while double bars are used to indicate peaks that have been truncated. The abbreviations s, d, t, at, dd, q, and m were used to signify singlet, doublet, triplet, apparent triplet, doublet of doublets, quartet, and multiplet, respectively.

High Resolution Mass Spectrometry (HRMS) – HRMS data were obtained on a Micromass AutoSpec Ultima Magnetic Sector mass spectrometer via electrospray ionization in negative ion mode.

UV-vis Spectroscopy – UV-vis spectra were taken on a Perkin-Elmer Lambda 850 UV-visible spectrometer. Calibration curves were measured at the λ_{max} for each compound. All experiments were run in triplicate at rt.

Preparation of 65 mM Borax Buffer – $Na_2B_4O_7{\cdot}H_2O$ (5.2 mmol) and NaOH (170 mmol) were dissolved in 80 mL of H_2O. The solution pH was determined to be 13 using a Beckman Coulter 3-in-1 pH Electrode.

Rheology - Rheological measurements were taken on an AR2000ex rheometer (TA Instruments) with a 25 mm serrated parallel plate. A gel (1.5x cgc) was loaded onto a serrated plate. The gap was then fixed at 300 μm. A solvent trap was used to limit solvent evaporation. The sample was pre-sheared under a stress of 0.1 Pa for 1 min before conducting the frequency sweep and oscillating stress sweep experiments. All measurements were repeated an average of 3 times to verify reproducibility. The frequency sweep experiment was performed under 0.1 Pa stress with a frequency range from 0.1 to 100 rad/s. The oscillating stress sweep experiment was performed at 1 Hz, with a stress range from 0.06 to 800 Pa (note that representative plots are shown in section VII).

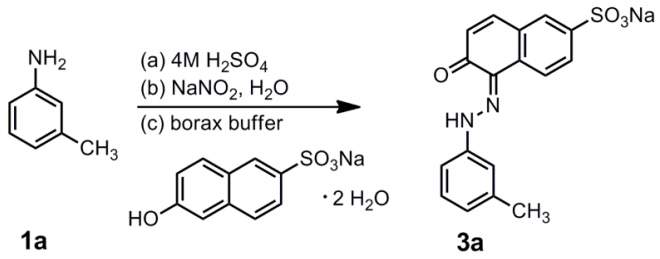
Optical Microscopy (OM) – OM was performed using a Nikon Eclipse 80i microscope under the transmission mode. The images were captured using a QICAM Fast 1394 Color digital camera mounted on the microscope and processed using the QCapture Pro v6.0 software. Gel samples were placed on a glass slide and covered with another glass slide to prevent solvent evaporation.

Scanning Electron Microscopy (SEM) – Wet gel samples were loaded onto a stainless steel SEM holder covered with copper tape and allowed to air dry overnight. Samples were then sputter-coated with Au for 2 min to reduce charge build-up during imaging. All gels were imaged using the high vacuum mode on a Hitachi S3200N SEM using a 15-KV accelerating voltage. The images were digitally recorded and processed using Adobe Photoshop.

Thermogravimetric Analysis (TGA) - TGA was performed on a TA instruments TGA Q50. Data were analyzed with TA Universal Analysis software Version 4.3 A. Thermal behavior of the samples were studied under a nitrogen purge at 10 °C/min heating rate. The temperature range was 25 – 400 °C/min.

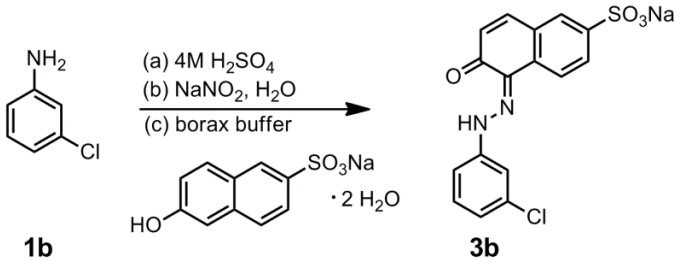
Elemental Analysis – Elemental samples were analyzed for carbon, hydrogen and nitrogen by Atlantic Microlabs. The water content calculation was based on deviation from expected C, H, and N values.

III. Synthetic Procedures



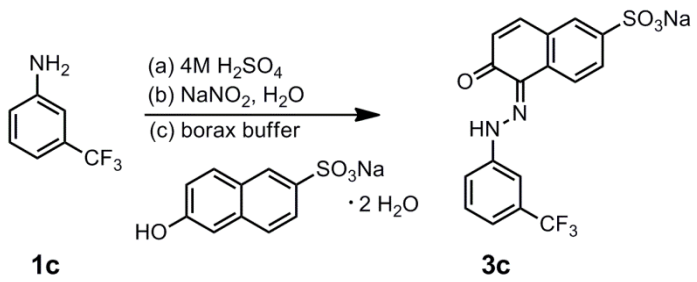
1a **3a**

3a: In a round-bottom flask equipped with a stir bar, *m*-toluidine (0.34 mL, 3.1 mmol) was dissolved in 4M H_2SO_4 (10 mL). In a separate 4 mL vial, $NaNO_2$ (0.210 g, 3.05 mmol) was dissolved in H_2O (2 mL). The solution of $NaNO_2$ was then added to the aniline solution and stirred for 2 min at rt. Then sodium 2-naphthol-6-sulfonate dihydrate (0.504 g, 1.79 mmol) dissolved in borax buffer (38 mL) was added to the reaction solution. Within 1 h a red-orange precipitate was observed and collected by filtration. Purification of the precipitate was carried out by Soxhlet extraction with acetone (7 d). The resulting solid percipitate was collected by filtration to give a red-orange solid (0.28 g, 43% yield). HRMS (ESI): Cald for $C_{17}H_{13}N_2O_4S$, 341.0602; found 341.0607. Elemental Analysis: Cald for $C_{17}H_{13}N_2O_4SNa$ with water content = 2.4%, C, 54.69; H, 3.78; N, 7.50; Found C, 54.66; H, 3.70; N, 7.39.



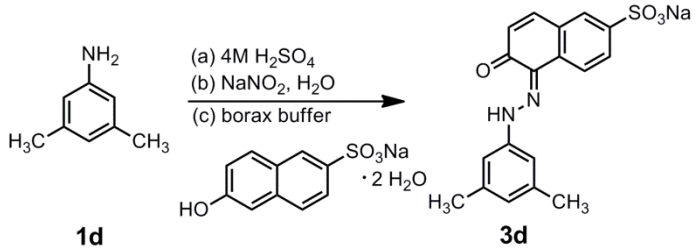
1b **3b**

3b: In a round-bottom flask equipped with a stir bar, 3-chloroaniline (0.32 mL, 3.0 mmol) was dissolved in 4M H_2SO_4 (10 mL). In a separate 4 mL vial, $NaNO_2$ (0.211 g, 3.05 mmol) was dissolved in H_2O (2 mL). The solution of $NaNO_2$ was then added to the aniline solution and stirred for 2 min at rt. Then sodium 2-naphthol-6-sulfonate dihydrate (0.501 g, 1.78 mmol) dissolved in borax buffer (38 mL) was added to the reaction solution. Within 1 h a red-orange precipitate was observed and collected by filtration. Purification of the precipitate was carried out by Soxhlet extraction with acetone (2 d). The solid percipitate collected was then further purified by Soxhlet extraction with acetonitrile (5 d). The resulting solid percipitate was collected by filtration to give a red-orange solid (0.153 g, 22% yield). HRMS (ESI): $C_{16}H_{10}ClN_2O_4S$, 361.0055; found 361.0061. Elemental Analysis: Cald for $C_{16}H_{10}ClN_2O_4SNa$ with water content = 6.6%, C, 46.67; H, 3.18; N, 6.80; Found C, 46.74; H, 3.21; N, 6.68.



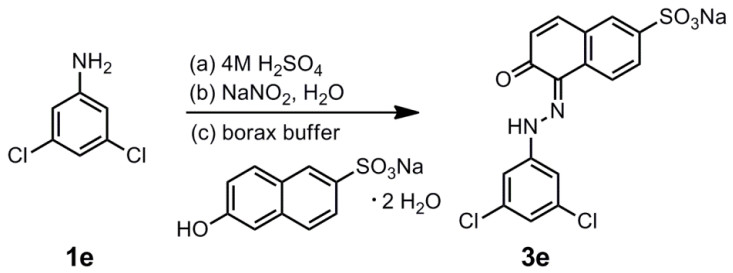
1c **3c**

3c: In a round-bottom flask equipped with a stir bar, 3-(trifluoromethyl)aniline (0.38 mL, 3.0 mmol) was dissolved in 4M H_2SO_4 (10 mL). In a separate 4 mL vial, $NaNO_2$ (0.211 g, 3.06 mmol) was dissolved in H_2O (2 mL). The solution of $NaNO_2$ was then added to the aniline solution and stirred for 2 min at rt. Then sodium 2-naphthol-6-sulfonate dihydrate (0.502 g, 1.78 mmol) dissolved in borax buffer (38 mL) was added to the reaction solution. Within 1 h a red-orange precipitate was observed and collected by filtration. Purification of the precipitate was carried out by Soxhlet extraction with acetone (3 d). The solid percipitate collected was then further purified by Soxhlet extraction with acetonitrile (2 d). The resulting solid percipitate was collected by filtration to give a red-orange solid (0.191 g, 25% yield). HRMS (ESI): Cald for $C_{17}H_{10}F_3N_2O_4S$, 395.0319; found 395.0324. Elemental Analysis: Cald for $C_{17}H_{10}F_3N_2O_4SNa$ with water content = 2.1%, C, 47.78; H, 2.59; N, 6.56; Found C, 47.55; H, 2.50; N, 6.48.



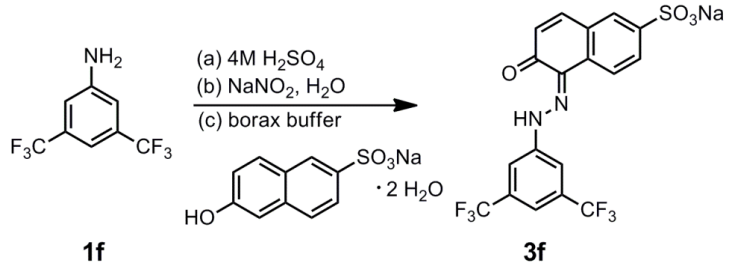
1d **3d**

3d: In a round-bottom flask equipped with a stir bar, 3,5-dimethylaniline (0.38 mL, 3.1 mmol) was dissolved in 4M H_2SO_4 (10 mL). In a separate 4 mL vial, $NaNO_2$ (0.212 g, 3.06 mmol) was dissolved in H_2O (2 mL). The solution of $NaNO_2$ was then added to the aniline solution and stirred for 2 min at rt. Then sodium 2-naphthol-6-sulfonate dihydrate (0.504 g, 1.79 mmol) dissolved in borax buffer (38 mL) was added to the reaction solution. Within 1 h a red-orange precipitate was observed and collected by filtration. Purification of the precipitate was carried out by Soxhlet extraction with acetone (9 d). The resulting solid percipitate was collected by filtration to give a red-orange solid (0.273 g, 40% yield). HRMS (ESI): Cald for $C_{18}H_{15}N_2O_4S$, 355.0758; found 355.0763. Elemental Analysis: Cald for $C_{18}H_{15}N_2O_4SNa$ with water content = 2.3%, C, 55.81; H, 4.16; N, 7.23; Found C, 56.04; H, 4.16; N, 7.11.



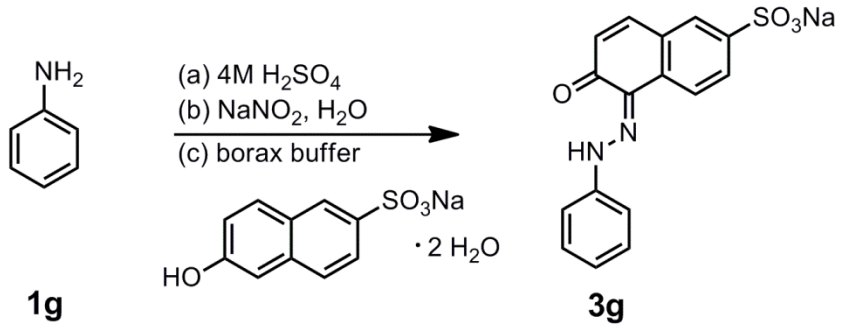
1e **3e**

3e: In a round-bottom flask equipped with a stir bar, 3,5-dichloroaniline (0.334 g, 2.04 mmol) was dissolved in 4M H_2SO_4 (10 mL). In a separate 4 mL vial, $NaNO_2$ (0.141 g, 2.03 mmol) was dissolved in H_2O (2 mL). The solution of $NaNO_2$ was then added to the aniline solution and stirred for 2 min at rt. Then sodium 2-naphthol-6-sulfonate dihydrate (0.500 g, 1.77 mmol) dissolved in borax buffer (38 mL) was added to the reaction solution. Within 1 h a red-orange precipitate was observed and collected by filtration. Purification of the precipitate was carried out by Soxhlet extraction with acetone/20% EtOH (2 d). The solid percipitate collected was then further purified by Soxhlet extraction with acetonitrile (4 d). The resulting solid percipitate was collected by filtration to give a red-orange solid (0.115 g, 15% yield). HRMS (ESI): Cald for $C_{16}H_9Cl_2N_2O_4S$, 394.9666; found 394.9670. Elemental Analysis: Cald for $C_{16}H_9Cl_2N_2O_4SNa$ with water content = 3.3%, C, 44.32; H, 2.46; N, 6.46; Found C, 44.15; H, 2.14; N, 6.16.



1f **3f**

3f: In a round-bottom flask equipped with a stir bar, 3,5-bis(trifluoromethyl)aniline (0.48 mL, 3.1 mmol) was dissolved in 4M H_2SO_4 (10 mL). In a separate 4 mL vial, $NaNO_2$ (0.212 g, 3.08 mmol) was dissolved in H_2O (2 mL). The solution of $NaNO_2$ was then added to the aniline solution and stirred for 2 min at rt. Then sodium 2-naphthol-6-sulfonate dihydrate (0.501 g, 1.77 mmol) dissolved in borax buffer (38 mL) was added to the reaction solution. Within 1 h a red-orange precipitate was observed and collected by filtration. Purification of the precipitate was carried out by Soxhlet extraction with acetone (2 d). The solid percipitate collected was then further purified by Soxhlet extraction with acetonitrile (3 d). The resulting solid percipitate was collected by filtration to give a red-orange solid (0.350 g, 40% yield). HRMS (ESI): Cald for $C_{18}H_9F_6N_2O_4S$, 463.0193; found 463.0198. Elemental Analysis: Cald for $C_{18}H_9F_6N_2O_4SNa$ with water content = 1.8%, C, 43.65; H, 2.03; N, 5.66; Found C, 43.40; H, 1.95; N, 5.59.



3g: In a round-bottom flask equipped with a stir bar, aniline (0.28 mL, 3.1 mmol) was dissolved in 4M H_2SO_4 (10 mL). In a separate 4 mL vial, $NaNO_2$ (0.21 g, 3.1 mmol) was dissolved in H_2O (2 mL). The solution of $NaNO_2$ was then added to the aniline solution and stirred for 2 min at rt. Then sodium 2-naphthol-6-sulfonate dihydrate (0.51 g, 1.8 mmol) dissolved in borax buffer (38 mL) was added to the reaction solution. After 30 min NaCl (2 equiv.) was added to help precipitate the product. Within 1 h a red-orange precipitate was observed and collected by filtration. Purification of the precipitate was carried out by Soxhlet extraction with acetone (2 d). The solid percipitate collected was then further purified by Soxhlet extraction with acetonitrile (6 d). The resulting solid percipitate was collected by filtration to give a red-orange solid (0.133 g, 21% yield). HRMS (ESI): Cald for $C_{16}H_{11}N_2O_4S$, 327.0445; found 327.0449. Elemental Analysis: Cald for $C_{16}H_{11}N_2O_4Na$, C, 54.86; H, 3.16; N, 8.00; Found C, 54.66; H, 3.27; N, 7.99.

V. ^{1}H and ^{13}C NMR Spectroscopic Data

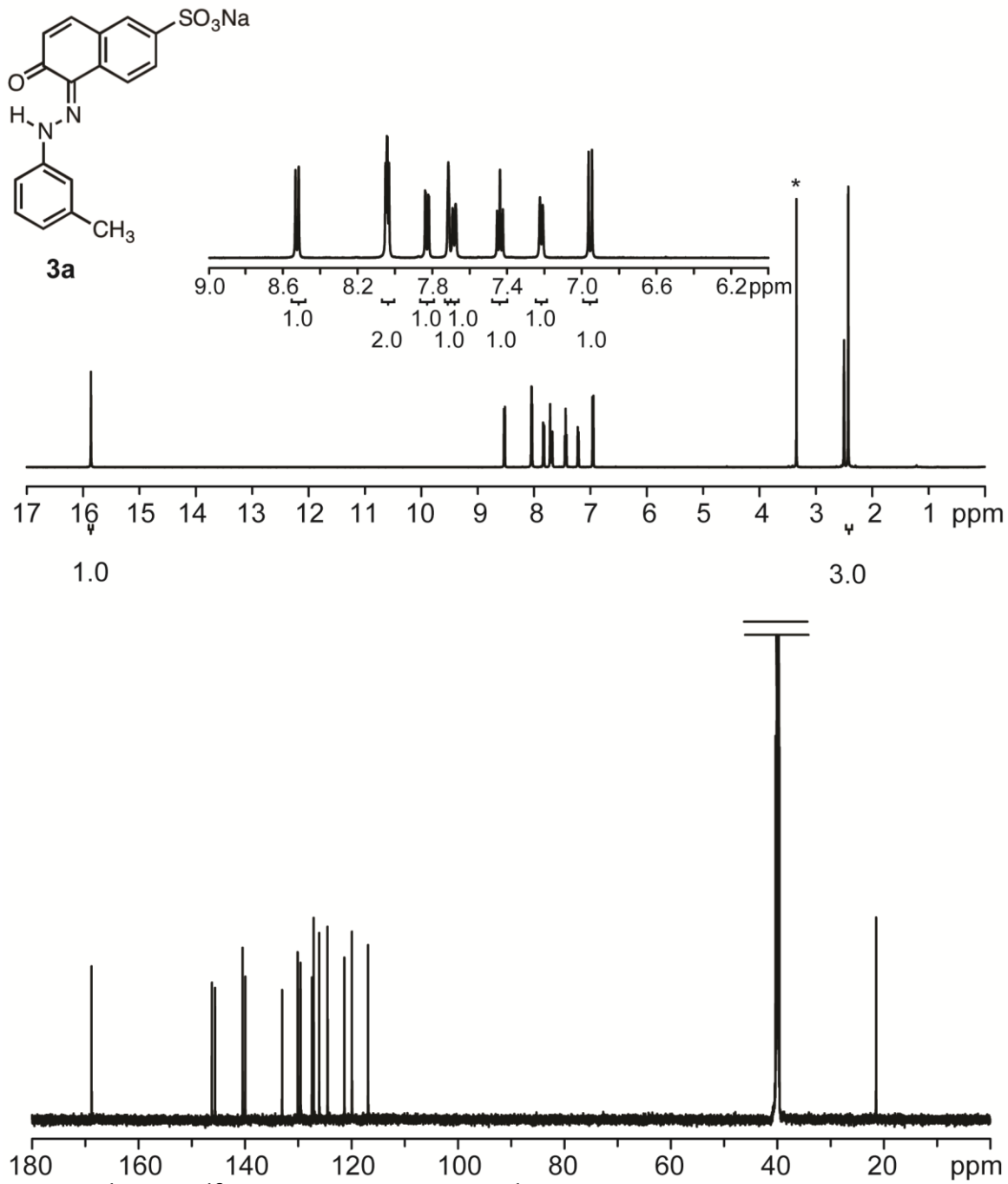


Figure S1. ^{1}H and ^{13}C NMR spectra of **3a**. ^{1}H NMR (500 MHz, DMSO-d_6) δ 15.86 (s, 1H), 8.53 (d, J = 8.7 Hz, 1H), 8.05 (m, 2 H), 7.84 (dd, J = 8.5, 1.6 Hz, 1H), 7.71 (s, 1H), 7.69 (d, J = 8.1 Hz, 1H), 7.45 (t, J = 7.8 Hz, 1H), 7.22 (d, J = 7.4 Hz, 1H), 6.96 (d, J = 9.5 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (176 MHz, DMSO-d_6) δ 168.81, 146.21, 145.61, 140.45, 139.94, 133.03, 130.10, 129.61, 129.56, 127.44, 127.09, 126.06, 124.49, 121.33, 119.91, 116.88, 21.44.

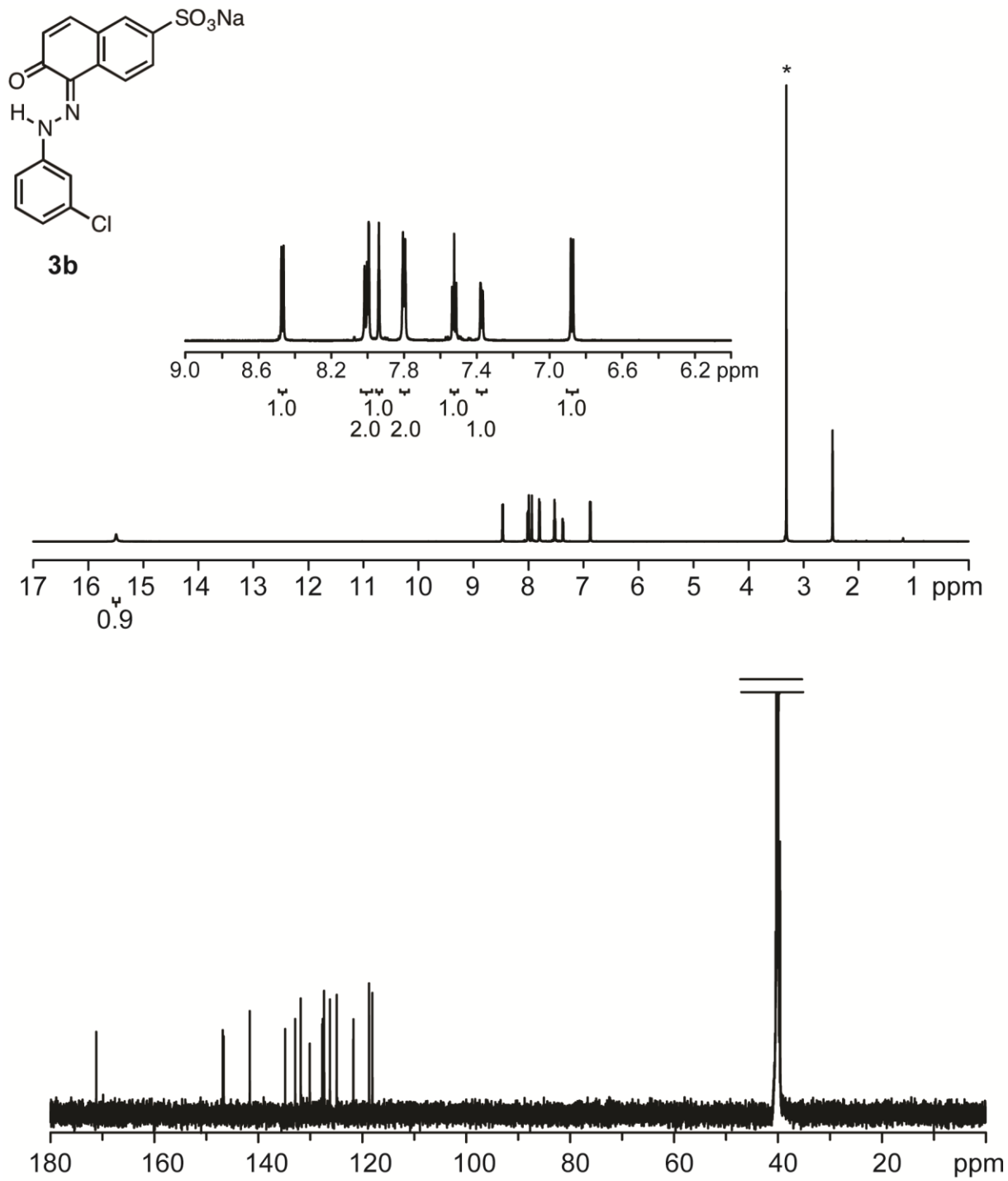


Figure S2. ^{1}H and ^{13}C NMR spectra of **3b**. ^{1}H NMR (700 MHz, DMSO-d_6) δ 15.52 (s, 1H), 8.48 (d, J = 8.9 Hz, 1H), 8.02 (m, 2H), 7.94 (t, J = 2.0 Hz, 1H), 7.81 (d, J = 8.5 Hz, 2H), 7.54 (t, J = 8.2 Hz, 1H), 7.38 (dd, J = 7.8, 1.4 Hz, 1H), 6.88 (d, J = 9.6 Hz, 1H). ^{13}C NMR (176 MHz, DMSO-d_6) δ 171.18, 146.83, 146.66, 141.65, 134.83, 132.91, 131.83, 130.09, 127.69, 127.62, 127.34, 126.20, 124.90, 121.70, 118.68, 118.04.

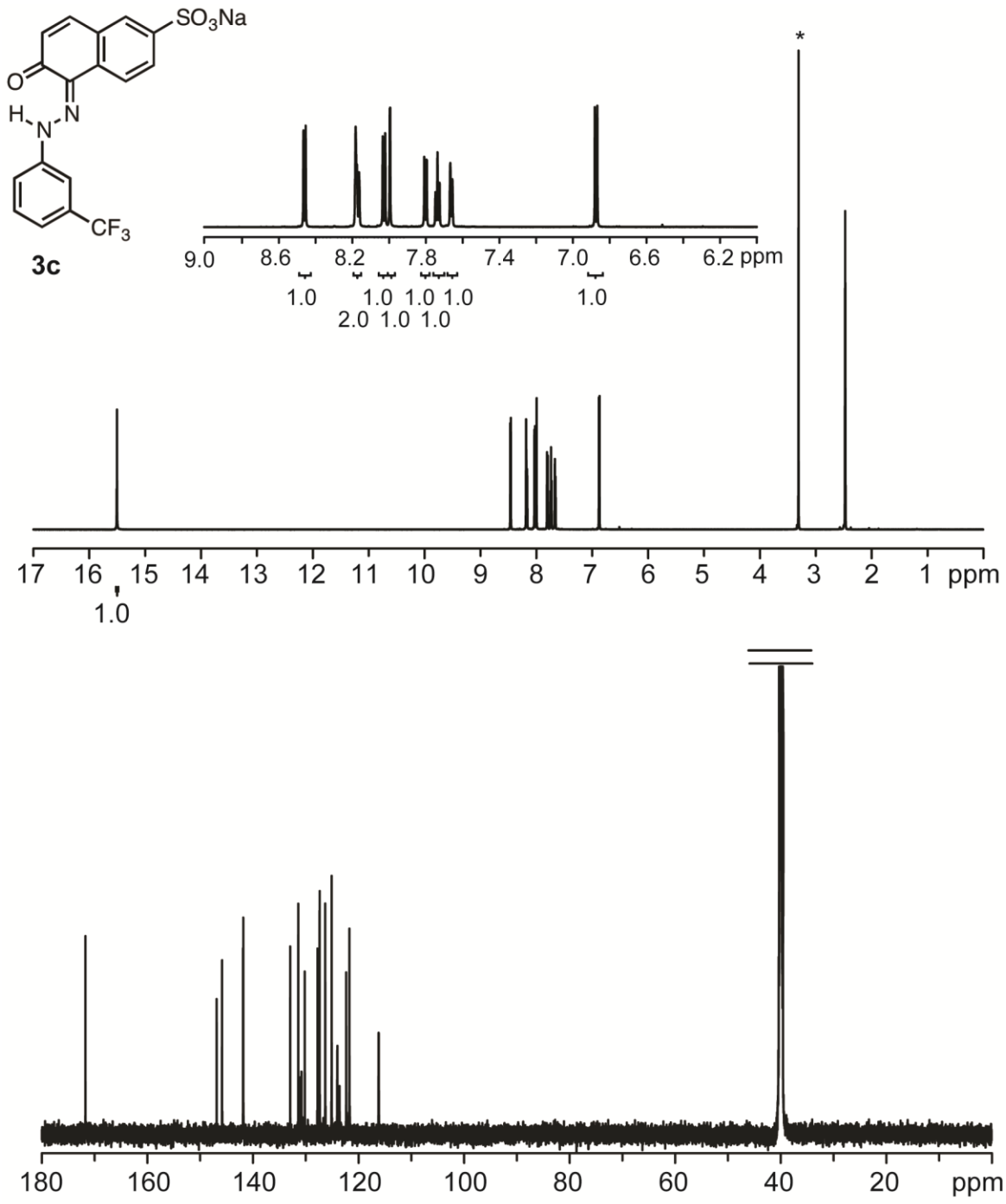


Figure S3. ^{1}H and ^{13}C NMR spectra of **3c**. ^{1}H NMR (500 MHz, DMSO-d_6) δ 15.50 (s, 1H), 8.47 (d, J = 8.5 Hz, 1H), 8.18 (m, 2H), 8.04 (d, J = 9.3 Hz, 1H), 8.00 (d, J = 1.7 Hz, 1H), 7.81 (dd, J = 8.4, 1.8 Hz, 1H), 7.75 (t, J = 8.1 Hz, 1H), 7.67 (d, J = 7.6 Hz, 1H) 6.88 (d, J = 9.4 Hz, 1H). ^{13}C NMR (176 MHz, DMSO-d_6) δ 171.52, 146.87, 145.84, 141.84, 132.95, 131.42, 131.17 (q, $J_{C\text{-}F}$ = 32.5 Hz), 130.24, 127.78, 127.38, 126.67 (q, $J_{C\text{-}F}$ = 271.5 Hz), 126.28, 125.00, 124.02 (q, $J_{C\text{-}F}$ = 3.8 Hz), 122.38, 121.68, 116.17 (q, $J_{C\text{-}F}$ = 3.4 Hz).

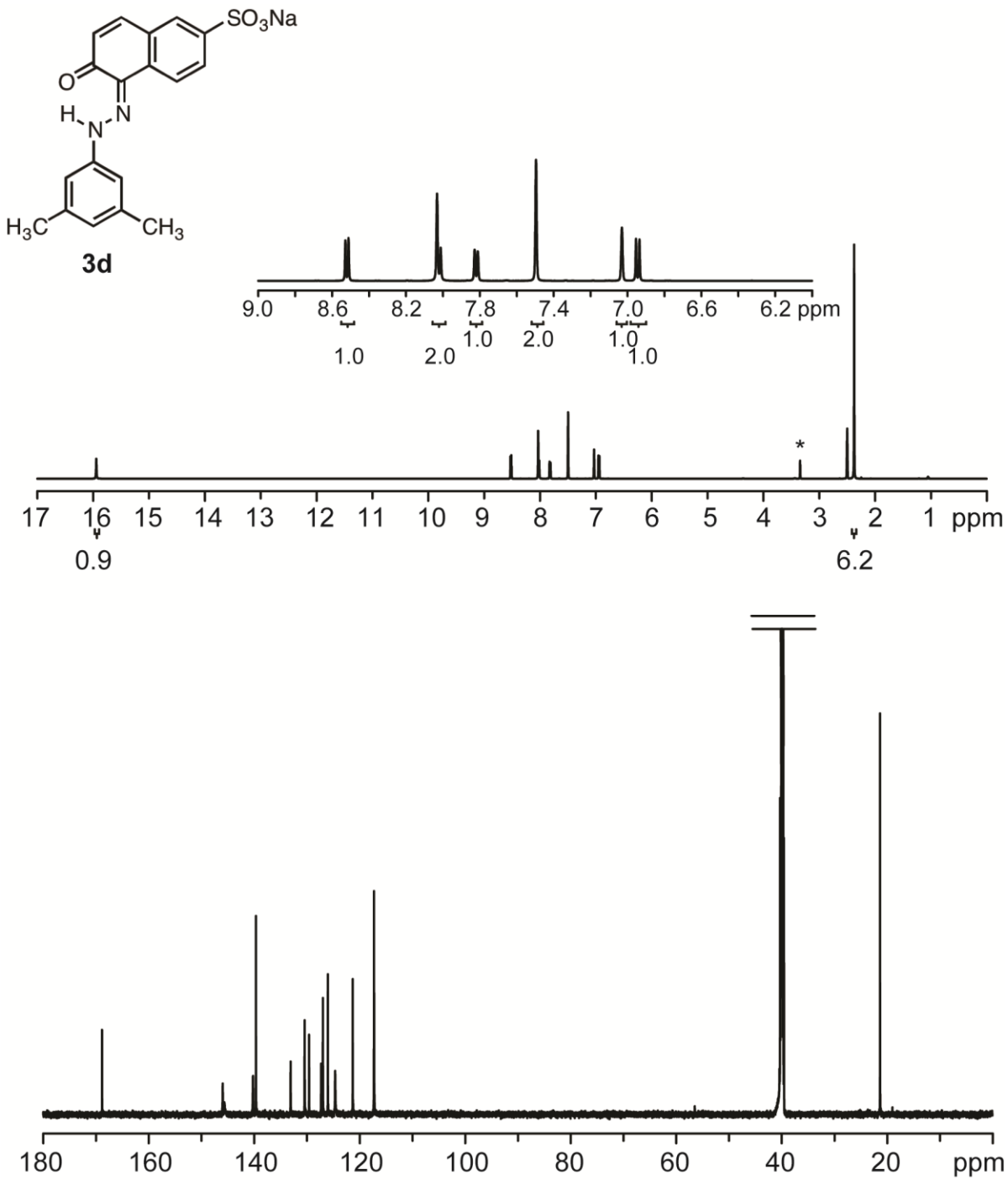


Figure S4. ^{1}H and ^{13}C NMR spectra of **3d**. ^{1}H NMR (500 MHz, DMSO-d_6) δ 15.94 (s, 1H), 8.53 (d, J = 8.7 Hz, 1H), 8.03 (m, 2H), 7.83 (d, J = 8.5 Hz, 1H), 7.50 (s, 2H), 7.03 (s, 1H), 6.95 (d, J = 9.6 Hz, 1H). ^{13}C NMR (176 MHz, DMSO-d_6) δ 168.83, 145.97, 145.67, 140.22, 139.66, 133.09, 130.43, 129.60, 127.31, 126.98, 126.04, 124.65, 121.31, 117.28, 21.35.

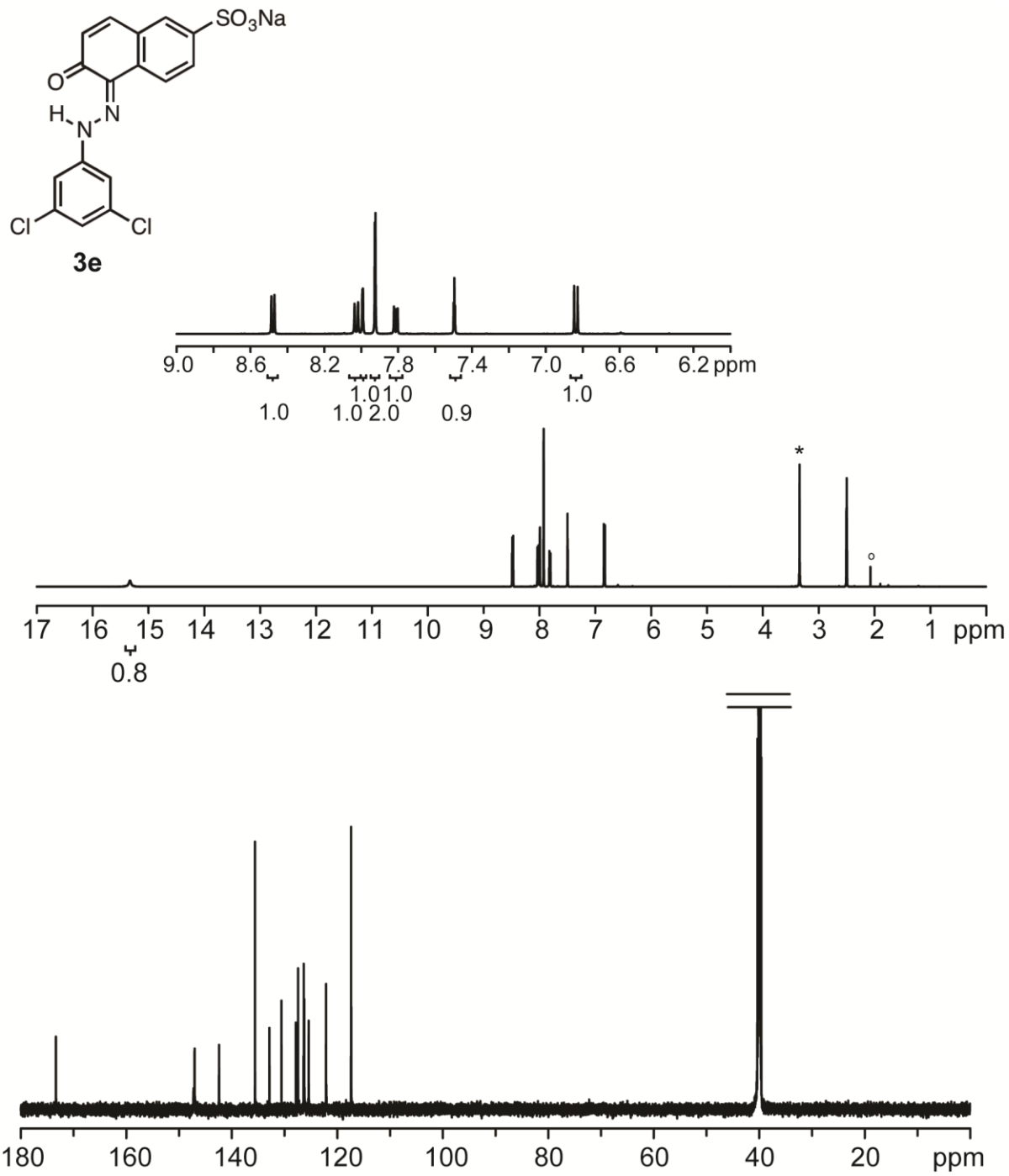


Figure S5. ^{1}H and ^{13}C NMR spectra of **3e**. ^{1}H NMR (500 MHz, DMSO-d_6) δ 15.49 (s, 1H), 8.49 (d, J = 9.2 Hz, 1H), 8.04 (d, J = 1.4 Hz, 1H), 7.93 (d, J = 2.0 Hz, 2H), 7.82 (dd, J = 8.4, 1.8 Hz, 1H), 7.50 (at, J = 2.0 Hz, 1H), 6.85 (d, J = 9.6 Hz, 1H). ^{13}C NMR (176 MHz, DMSO-d_6) δ 173.33, 147.23, 147.04, 142.41, 135.60, 132.86, 130.57, 127.85, 127.43, 126.36, 126.25, 125.42, 122.12, 117.37. Note: O indicates residual acetonitrile.

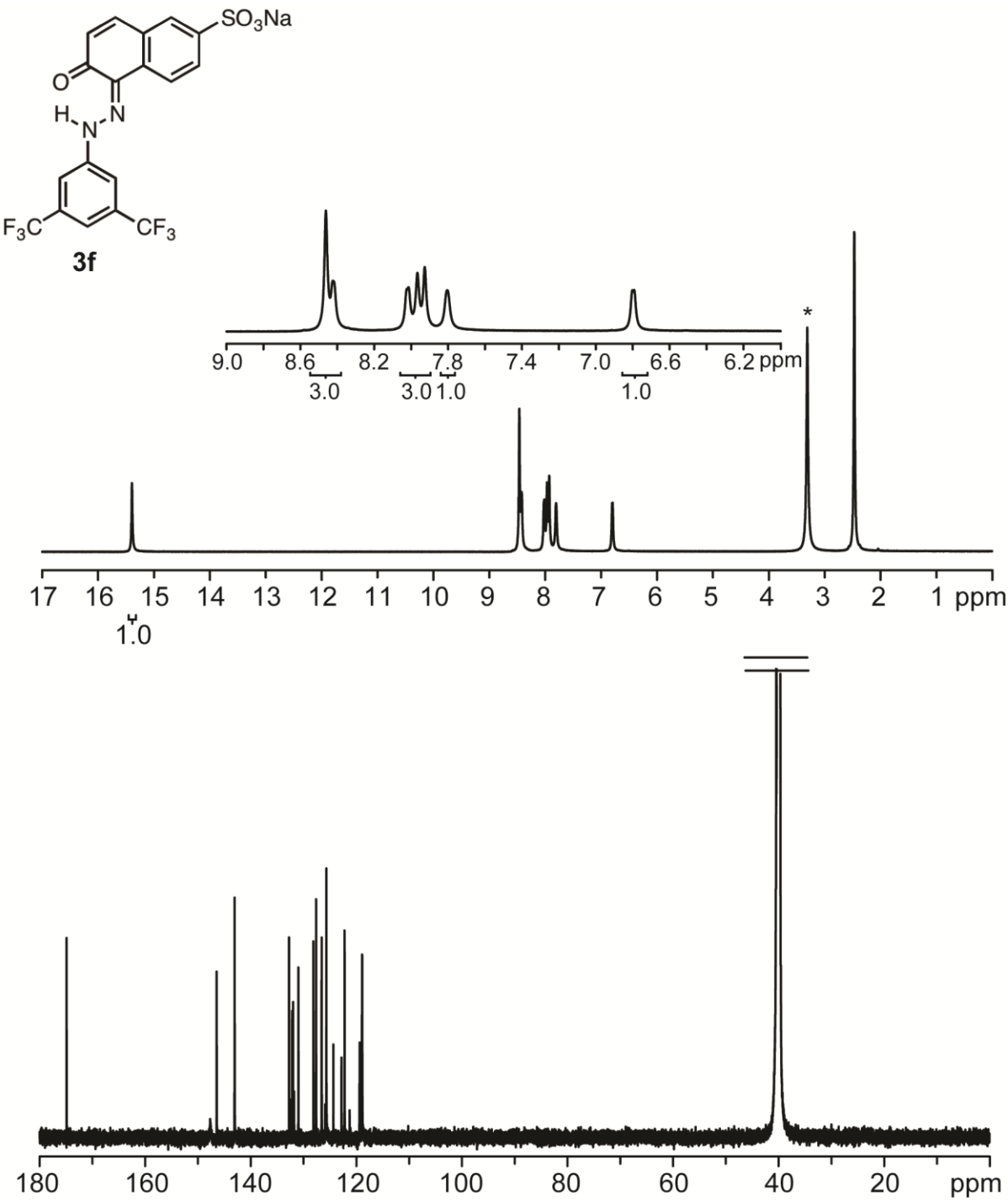


Figure S6. ^{1}H and ^{13}C NMR spectra of **3f**. ^{1}H NMR (700 MHz, DMSO-d_6) δ 15.39 (s, 1H), 8.46 (m, 3H), 8.02 (m, 3H), 7.81 (s, 1H), 6.80 (d, J = 7.7 Hz, 1H). ^{13}C NMR (176 MHz, DMSO-d_6) δ 174.87, 147.76, 146.44, 143.05, 132.73, 132.34 (q, $J_{C\text{-}F}$ = 33.1 Hz), 130.97, 128.12, 127.62, 126.55, 125.90 (q, $J_{C\text{-}F}$ = 274.1 Hz), 125.66, 122.22, 119.35, 118.89.

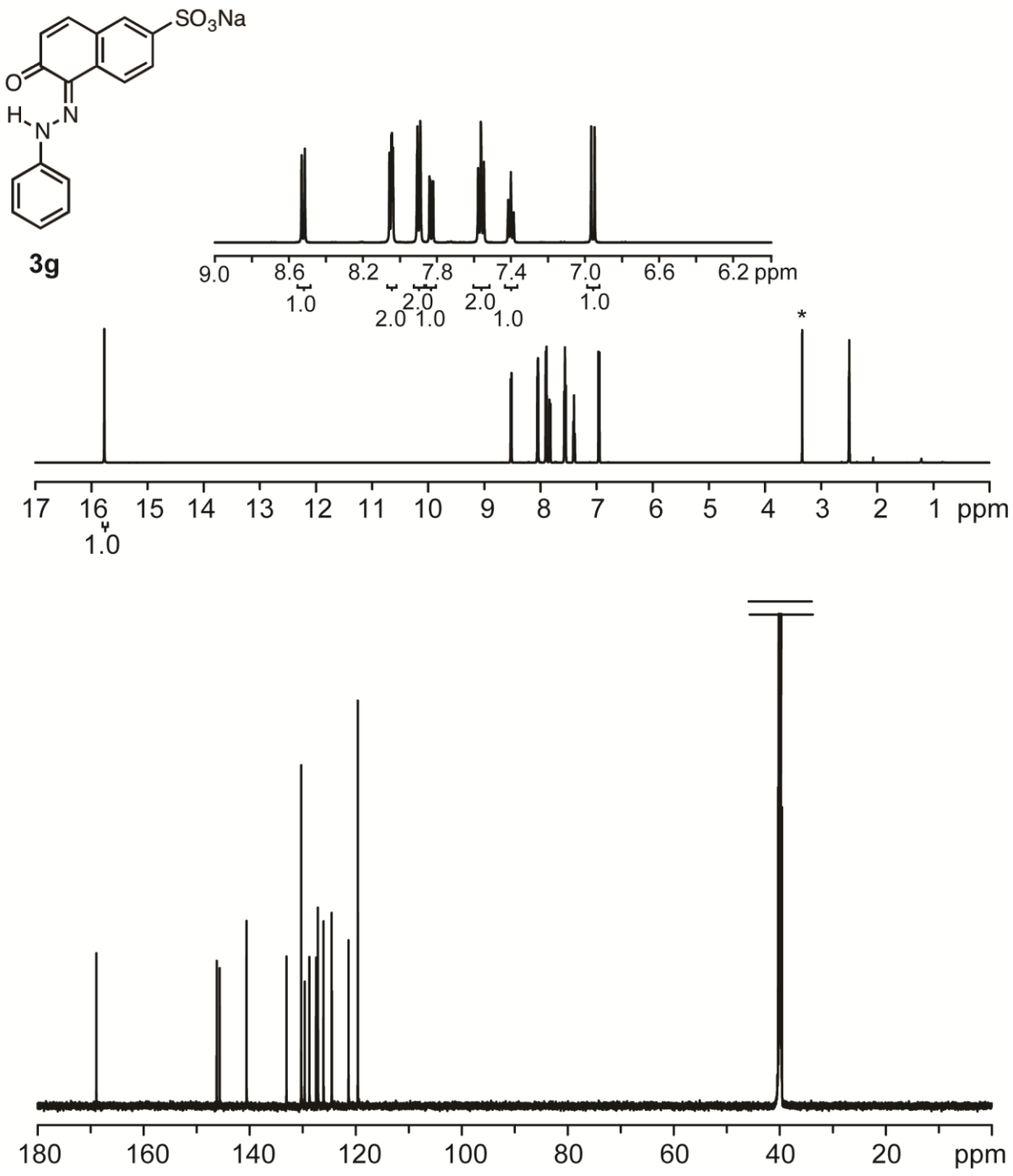


Figure S7. ^{1}H and ^{13}C NMR spectra of **3g**. ^{1}H NMR (500 MHz, DMSO-d_6) δ 15.78 (s, 1H), 8.53 (d, J = 8.6 Hz, 1H), 8.06 (m, 2H), 7.91 (d, J = 8.6 Hz, 2H), 7.84 (dd, J = 6.5, 1.7 Hz, 1H), 7.59 (at, J = 7.7 Hz, 2H), 7.42 (at, J = 7.2 Hz, 1H), 6.97 (d, J = 9.3 Hz, 1H). ^{13}C NMR (176 MHz, DMSO-d_6) δ 168.92, 146.21, 145.64, 140.59, 133.05, 130.28, 129.61, 128.73, 127.47, 127.12, 126.06, 124.51, 121.35, 119.60.

V. Determination of water in sodium 2-naphthol-6-sulfonate hydrate

Sodium 2-naphthol-6-sulfonate hydrate was purchased from TCI America as an unknown hydrate. TGA was performed to determine the average amount of water.

Sample Preparation Procedure **-** A sample of sodium 2-napthol-6-sulfonate hydrate was anaylzed by loading a small amount (2.809 mg) onto a platinum TGA pan and held under a nitrogen purge until dry, which was indicated by stabilization of the sample weight.

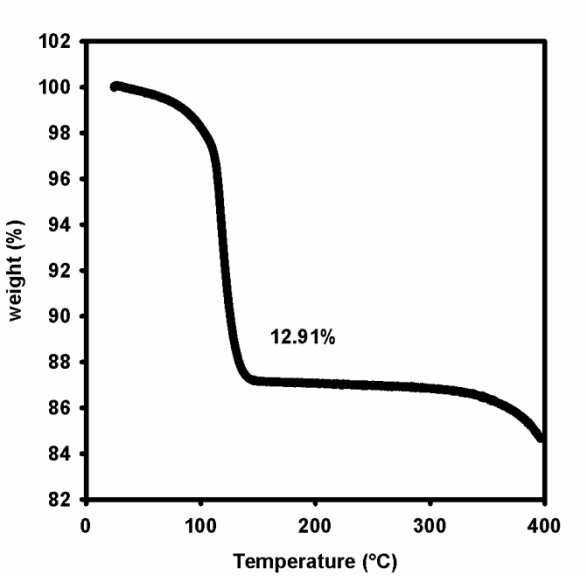


Figure S8. TGA of sodium 2-napthol-6-sulfonate hydrate.

Analysis of the above results indicated that sodium 2-napthol-6-sulfonate hydrate had an average of 2.024 H_2O per molecule of sodium 2-napthol-6-sulfonate hydrate. For the synthetic procedures, an average of 2 H_2O molecules was used.

VI. Gel Screening

Gel Screening and Critical Gel Concentration (cgc) Procedure – The cgc was determined by adding a known amount of gelator **3a–3g** (approximately 7-16 mg) into a 4 mL vial containing 1 mL of solvent. The vial was capped, heated to dissolve the solid, and allowed to cool with approximately 10 s of sonication in a rt water bath. If the resulting gel was stable-to-inversion, then 0.1 mL of solvent was added and the procedure was repeated until the gel was no longer stable-to-inversion. Sonication was not performed with **3d** as it disrupted gel formation.

Table S1. Summary of cgc data.[a]

	cgc (mM)	
compound	borax buffer	EtOH/borax buffer (9/1 v/v)
3a	Precipitate	23.5 ± 0.4
3b	29.4 ± 0.9[b]	43 ± 3
3c	24.2 ± 0.8	Precipitate
3d	Precipitate	35.5 ± 0.2
3e	21.3 ± 0.5	16.7 ± 0.6
3f	27 ± 1	Precipitate
3g	Soluble	30.0 ± 0.5

[a] Standard deviation was determined by an average of 3 runs. Gelation of each compound was tested up to 2 wt%. Precipitate in the above table refers to the observation of any amount of precipitate in the gelation media. The Cgc assumes the nonhydrated molecular weight of the product.
[b] Solution was 65 mM borax buffer:4M H_2SO_4:H_2O (7.6:2:0.4) (v/v/v)

Representative procedure for in situ detection of NO_2^- – In a 4 mL vial, **1e** (2.0 mg, 0.012 mmol, 1.1 equiv) was suspended in H_2SO_4 (0.2 mL, 4M). Then H_2O (40 µL) containing $NaNO_2$ (0.76 mg, 0.011 mmol, 1.0 equiv) was added. The vial was shaken for 30 s and let stand to react. After 10 min, sodium 2-napthol-6-sulfonate dihydrate (3.5 mg, 0.012 mmol, 1.1 equiv) dissolved in borax buffer (0.76 mL) was added and a color change from slight yellow to red-orange was observed. The vial was heated with a heat gun until all gelator was dissolved and then allowed to cool to rt.

*Determination of cgc at different pH for **3e*** – 65 mM borax buffer and sulfuric acid (18 M) were used to make solutions at a pH of 13, 9, and 6. A Beckman Coulter 3-in-1 pH Electrode was used to determine the pH. At each pH the cgc of **3e** was determined using the gel screening and cgc procedure.

Table S2. Summary of cgc data for **3e** at different pH.[a]

cgc of **3e** (mM)	
pH	
13	21.3 ± 0.5
9	9.6 ± 0.3
6	9.8 ± 0.3
Insitu (9)	9.3[b]

[a] The standard deviation was determined by an average of 3 runs. The cgc assumes the nonhydrated molecular weight of the product.
[b] See representative procedure for in situ detection of NO_2^-. The cgc was calculated based on a conversion of 85% (see section X)

VII. Gel Rheological Data

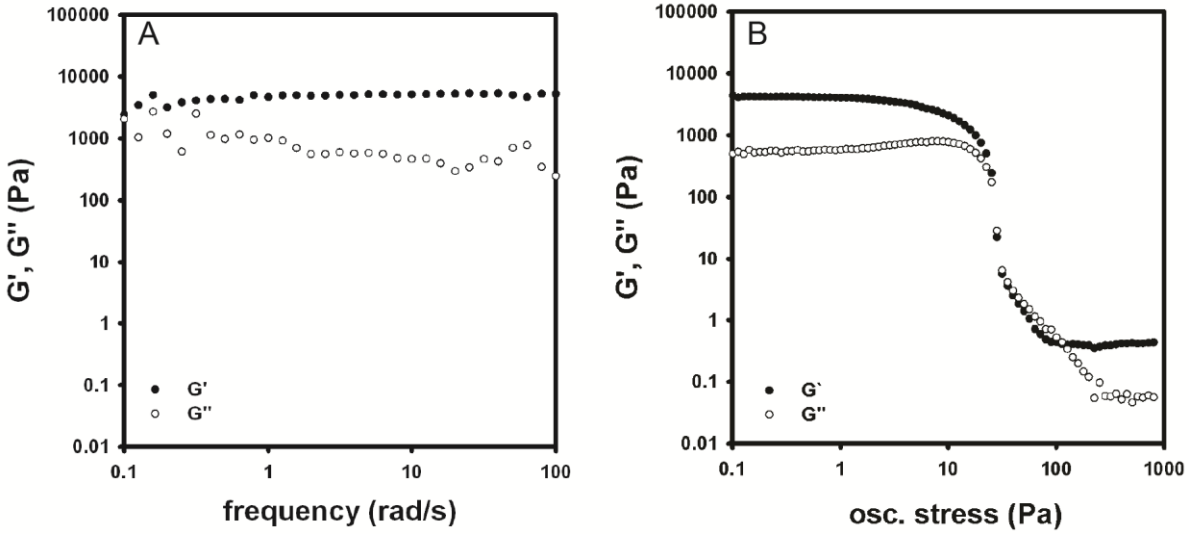


Figure S9. (A) Frequency sweep and (B) oscillating stress sweep of a gel of **3a** (50 mM in EtOH/borax buffer 9/1 (v/v)).

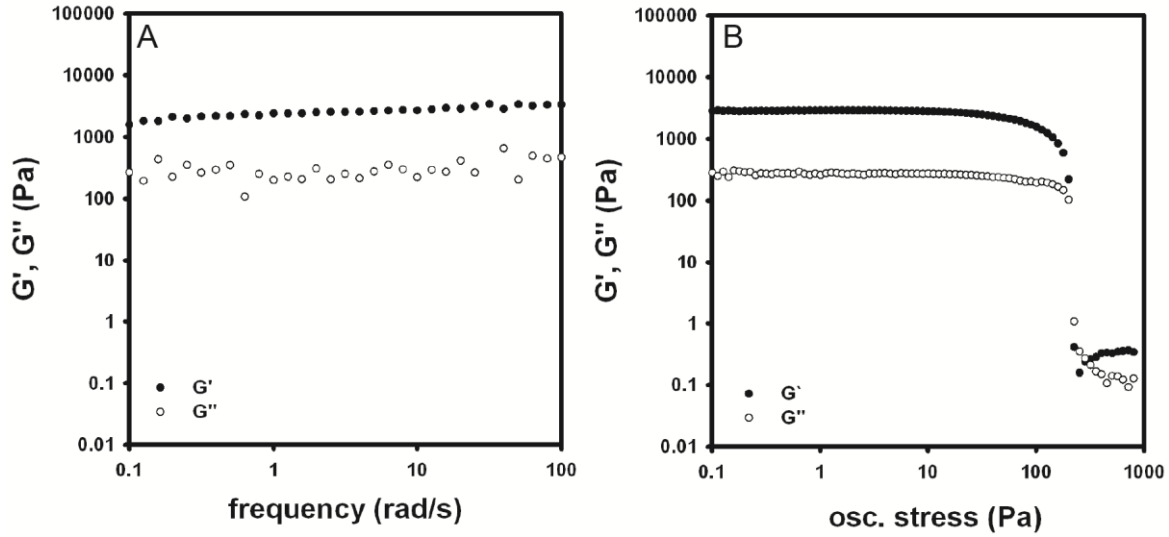


Figure S10. (A) Frequency sweep and (B) oscillating stress sweep of a gel of **3c** (36 mM in borax buffer).

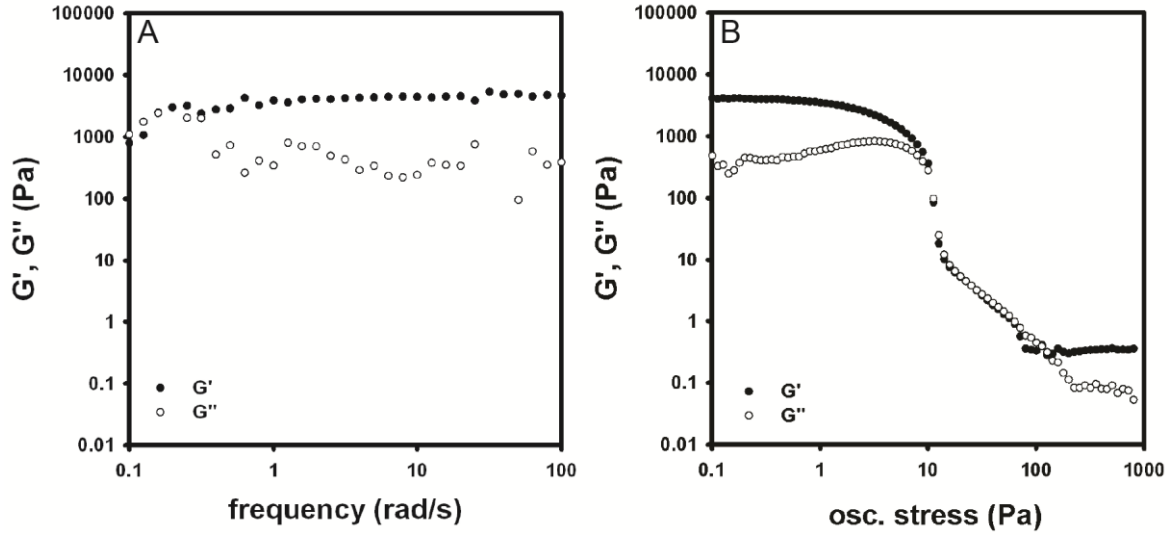


Figure S11. (A) Frequency sweep and (B) oscillating stress sweep of a gel of **3d** (53 mM in EtOH/borax buffer 9/1 (v/v)).

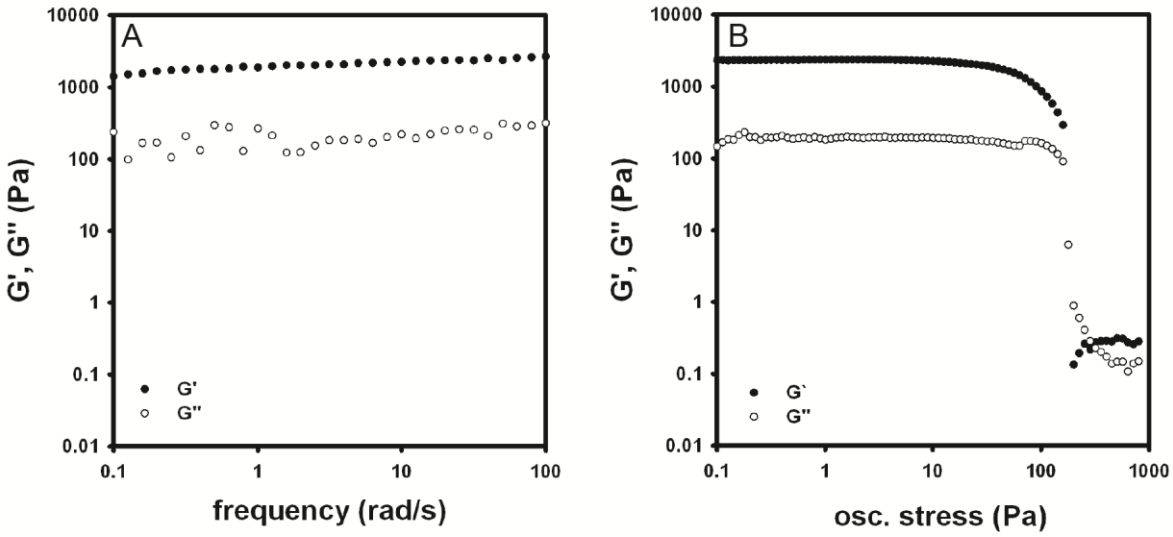


Figure S12. (A) Frequency sweep and (B) oscillating stress sweep of a gel of **3e** (32 mM in borax buffer).

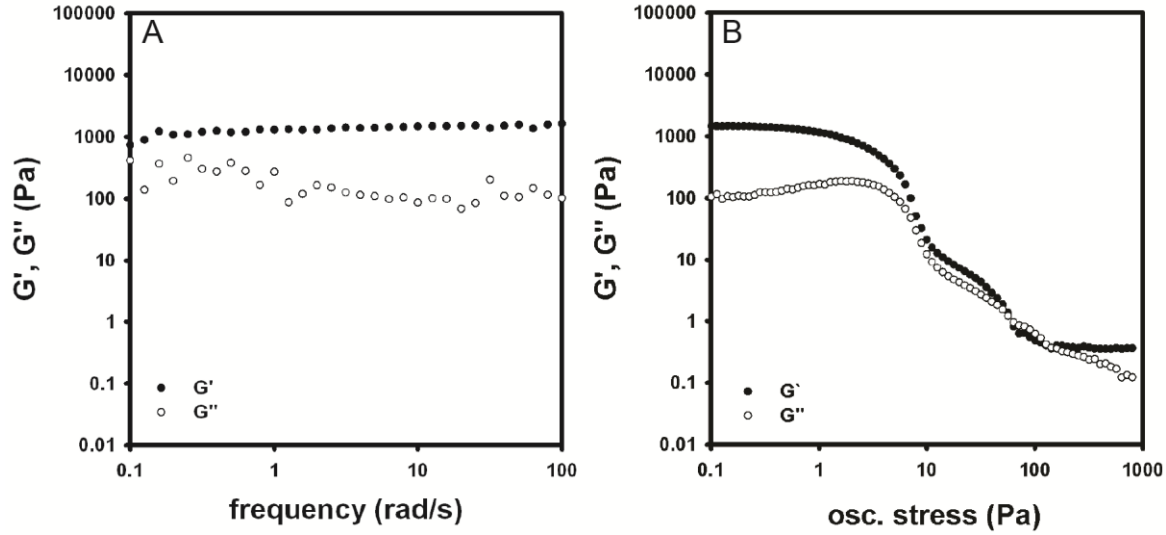


Figure S13. (A) Frequency sweep and (B) oscillating stress sweep of a gel of **3f** (42 mM in borax buffer).

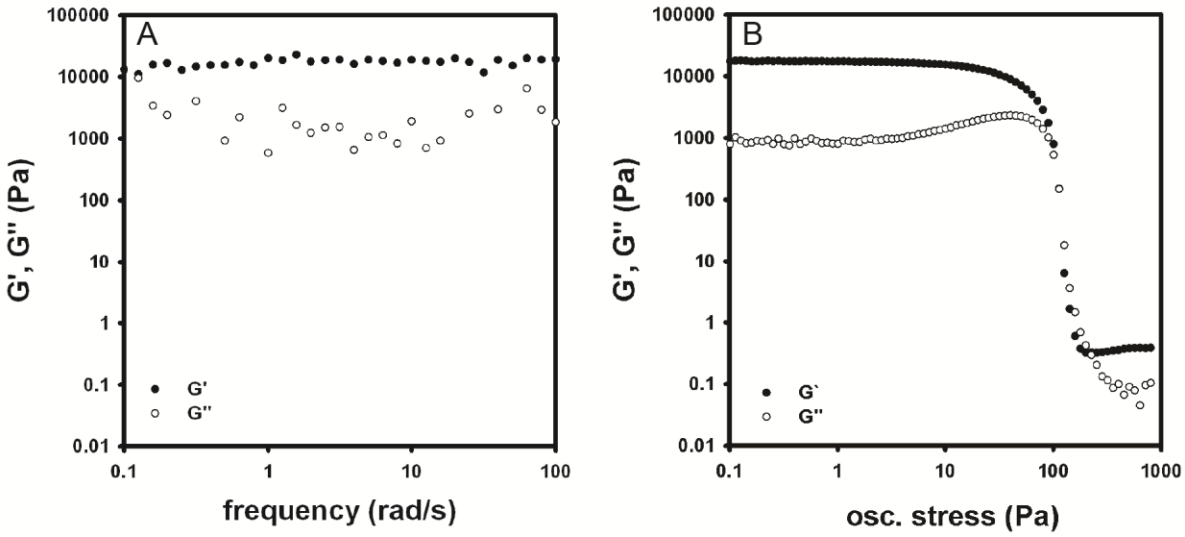


Figure S14. (A) Frequency sweep and (B) oscillating stress sweep of a gel of **3g** (45 mM in EtOH/borax buffer 9/1 (v/v)).

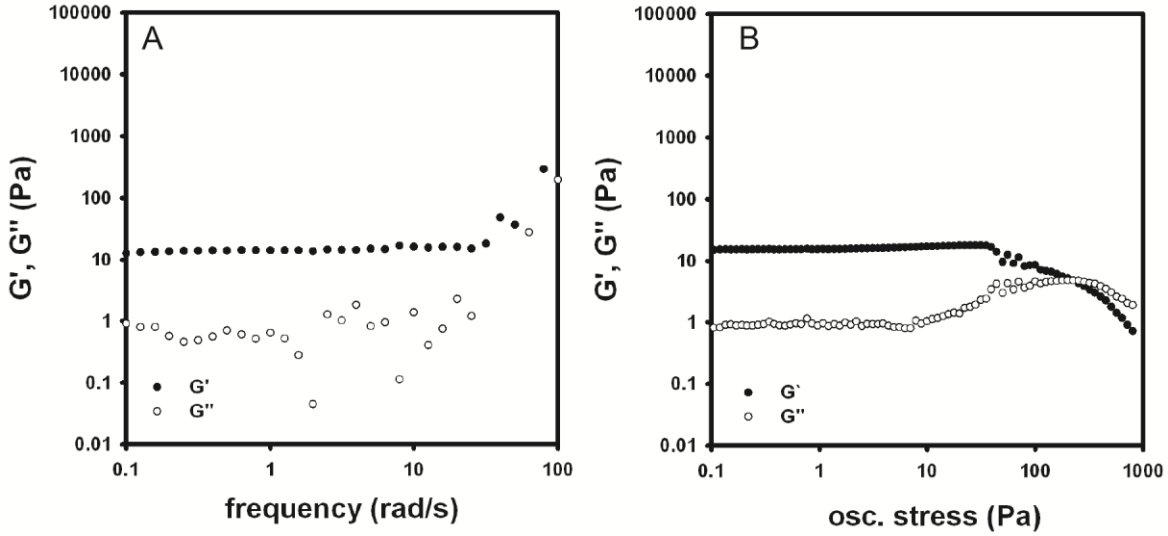


Figure S15. (A) Frequency sweep and (B) oscillating stress sweep of a gel of **3b** formed under in situ conditions at cgc (in borax buffer). See section VI for the in situ procedure.

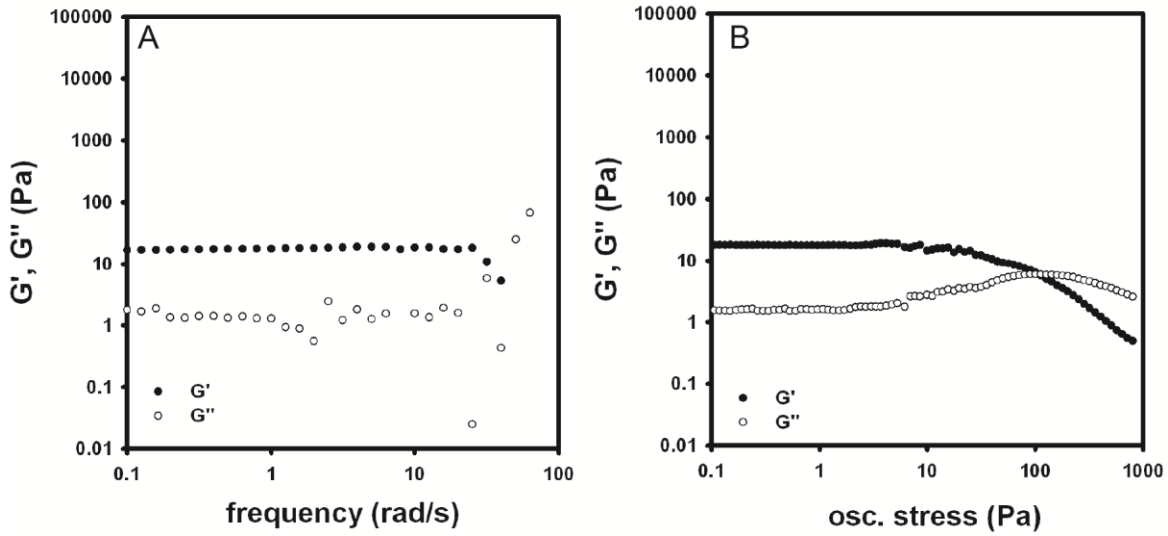


Figure S16. (A) Frequency sweep and (B) oscillating stress sweep of a gel of **3c** formed under in situ conditions at cgc (in borax buffer). See section VI for the in situ procedure.

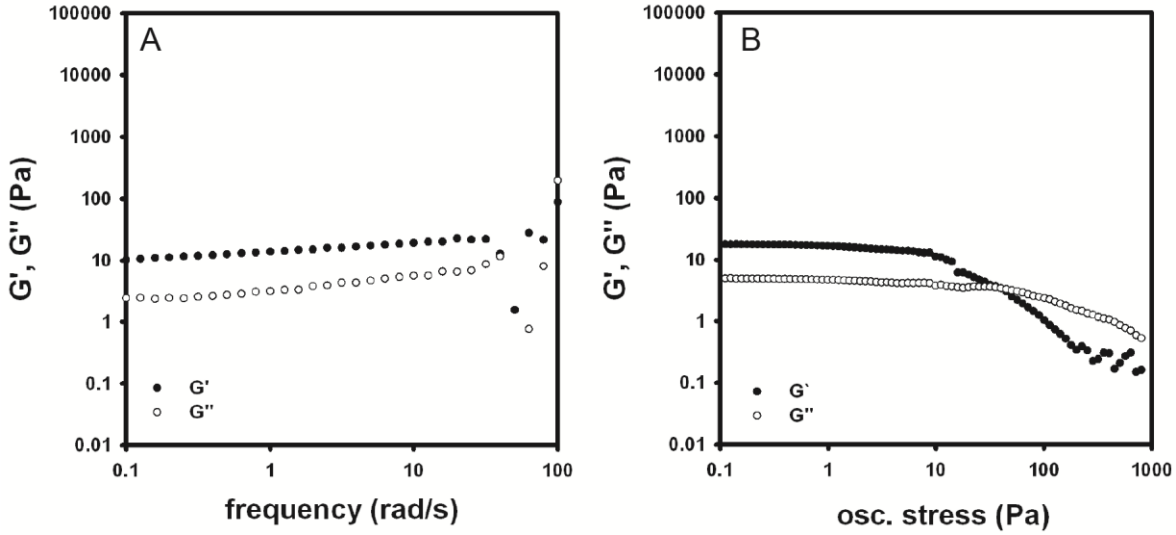


Figure S17. (A) Frequency sweep and (B) oscillating stress sweep of a gel of **3e** formed under in situ conditions at cgc (in borax buffer). See section VI for the in situ procedure.

Rheology of **3e** in situ gels with 1, 2, and 3 equiv of NO_2^-

Representative procedure of gel formation at 1 equiv of NO_2^-

Preparation of stock solutions

1e *solution (80.2 mM)* – **1e** (26.0 mg, 0.160 mmol) was dissolved in H_2SO_4 (2.0 mL, 4 M).

Sodium nitrite solution (405 mM) – $NaNO_2$ (12.3 mg, 0.178 mmol) was dissolved in H_2O (0.44 mL).

Sodium 2-naphthol-6-sulfonate dihydrate (21.4 mM) – Sodium 2-naphthol-6-sulfonate dihydrate (46.1 mg, 0.163 mmol) was dissolved in borax buffer (7.6 mL, 65 mM).

Representative procedure for in situ detection of NO_2^- - In a 4 mL vial, $NaNO_2$ solution (40 µL, 405 mM) was reacted with the **1e** solution (0.2 mL, 80.2 mM). The vial was shaken for 30 s and let stand to react for 10 min. Then the sodium 2-naphthol-6-sulfonate dihydrate solution (0.76 mL, 21.4 mM) was added and a color change from slight yellow to red-orange was observed. The vial was heated with a heat gun until all compounds were dissolved and then allowed to cool to rt. The vial was inverted to confirm stable gel formation.

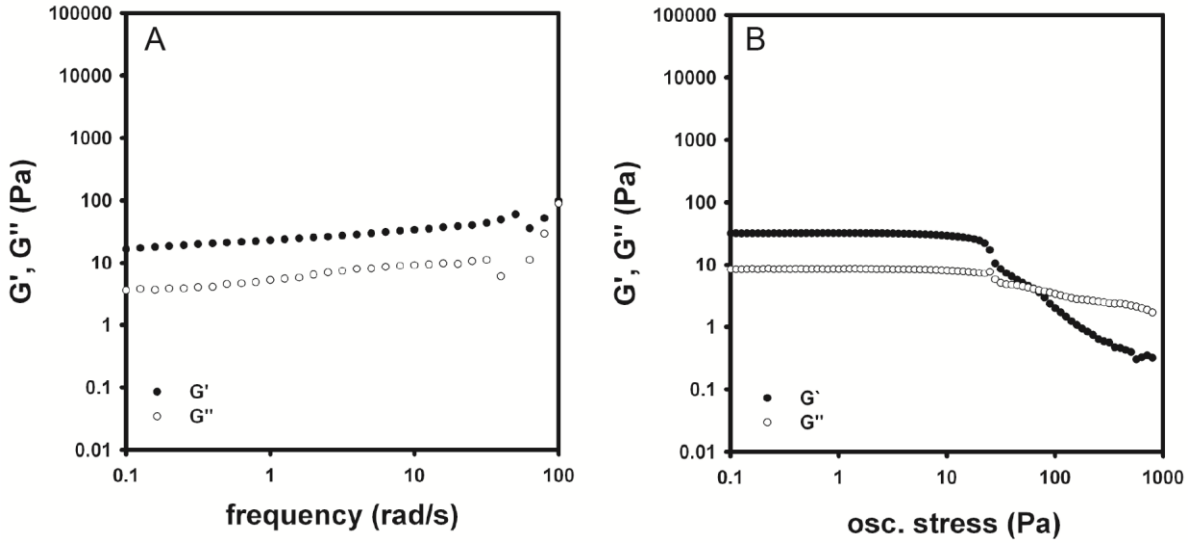


Figure S18. (A) Frequency sweep and (B) oscillating stress sweep of a gel of **3e** formed under in situ conditions at 1.5x cgc (in borax buffer) with 1 equiv of sodium nitrite.

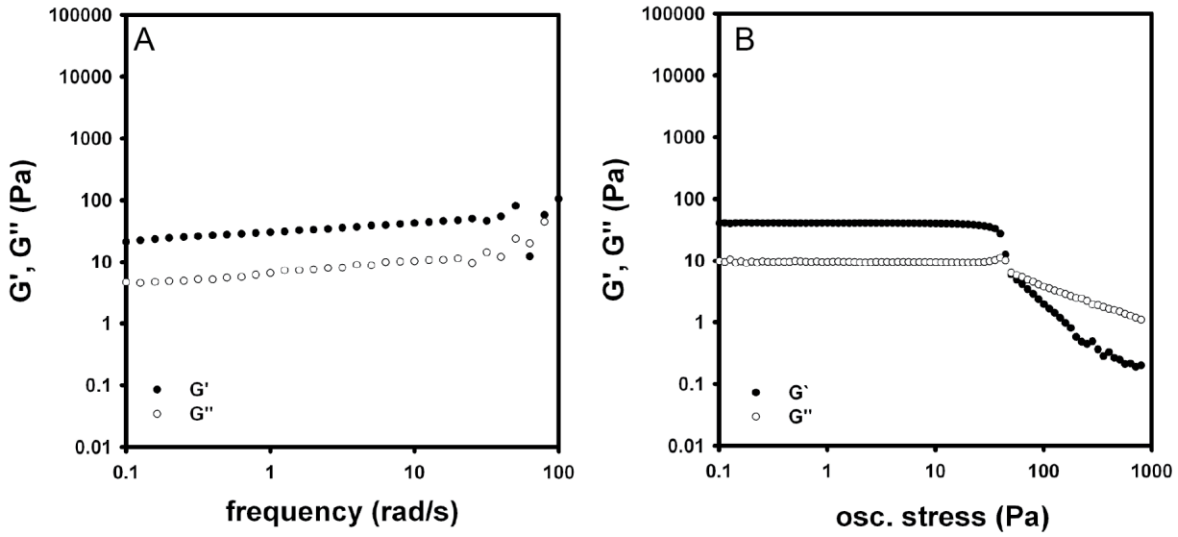


Figure S19. (A) Frequency sweep and (B) oscillating stress sweep of a gel of **3e** formed under in situ conditions at 1.5x cgc (in borax buffer) with 2 equiv of sodium nitrite.

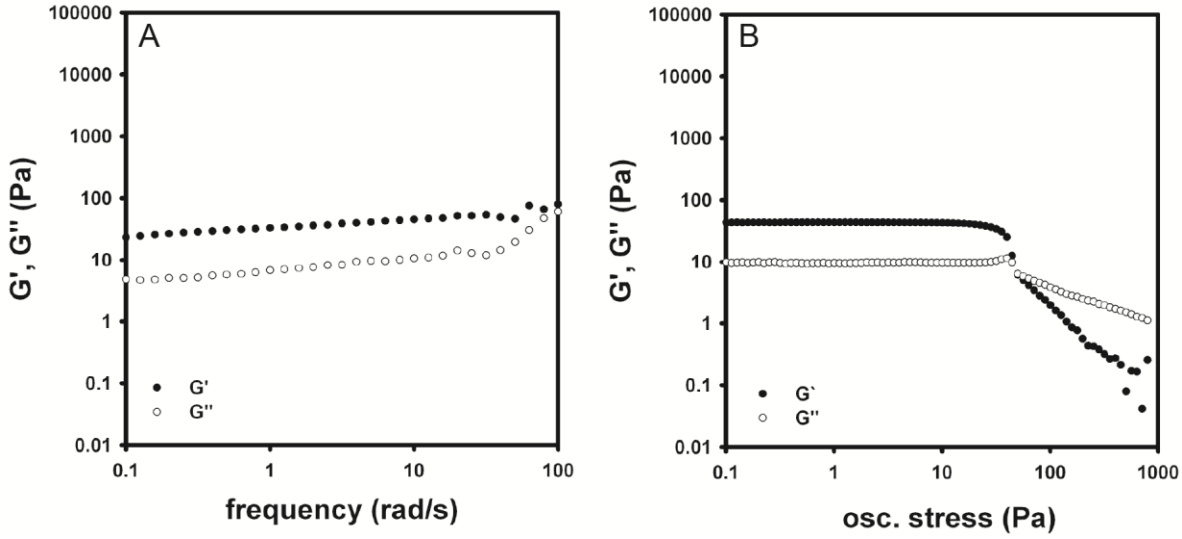


Figure S20. (A) Frequency sweep and (B) oscillating stress sweep of a gel of **3e** formed under in situ conditions at 1.5x cgc (in borax buffer) with 3 equiv of sodium nitrite.

VIII. Scanning Electron and Optical Microscopy Images

*SEM and OM of **3c*** - Gel fibers for **3c** were not observable within the range of the OM. SEM of gel **3c** only showed salt under conditions used (see section II).

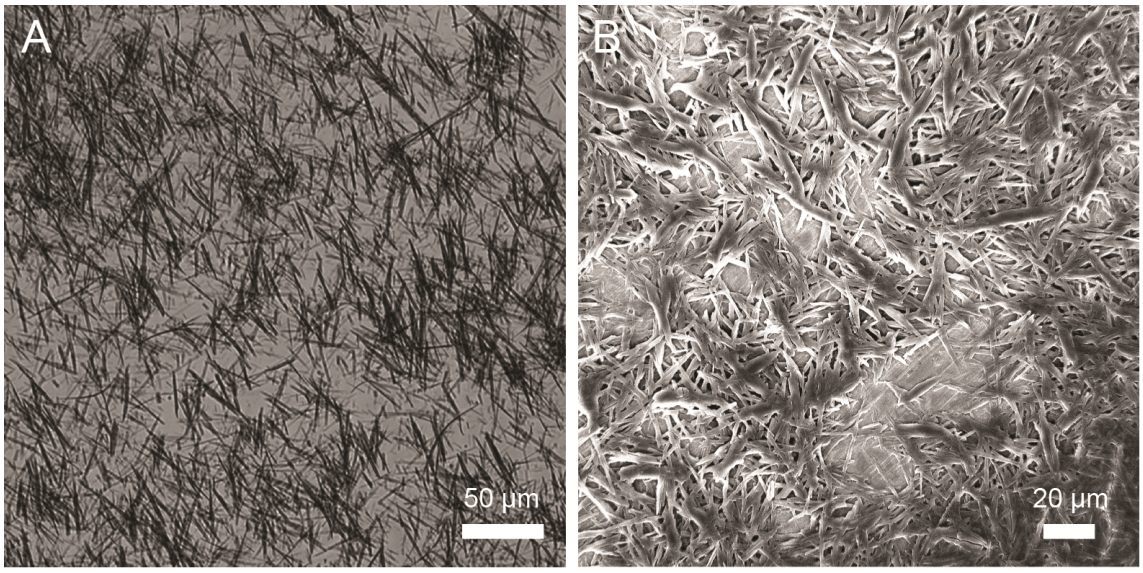


Figure S21. (A) OM and (B) SEM image of a gel of **3a** formed from purified material (44 mM in EtOH/borax buffer (9/1, v/v)).

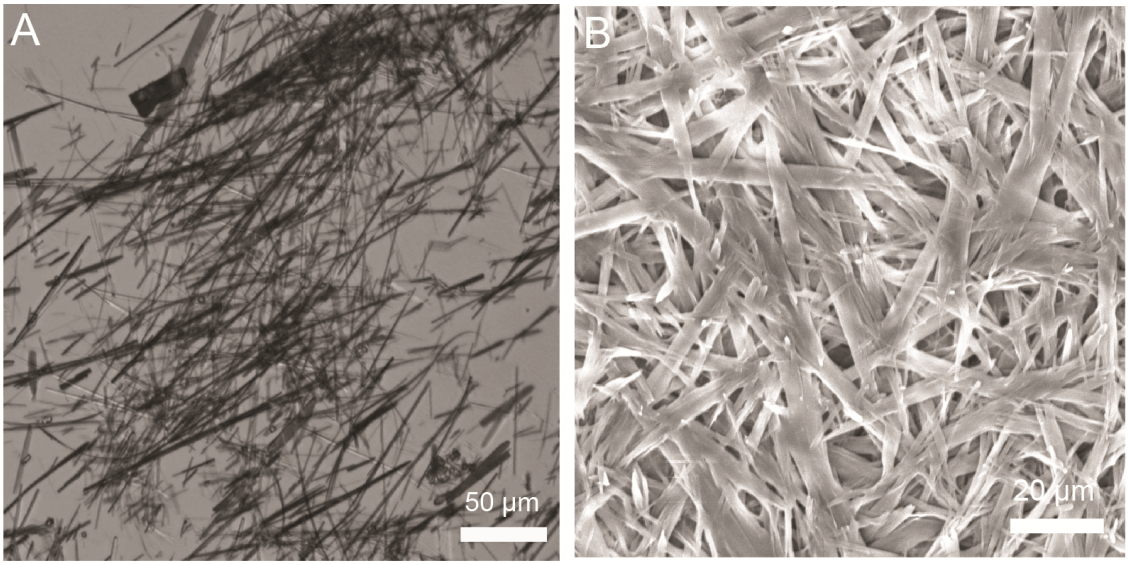


Figure S22. (A) OM and (B) SEM image of a gel of **3b** formed from purified material (38 mM in EtOH/borax buffer (9/1, v/v)).

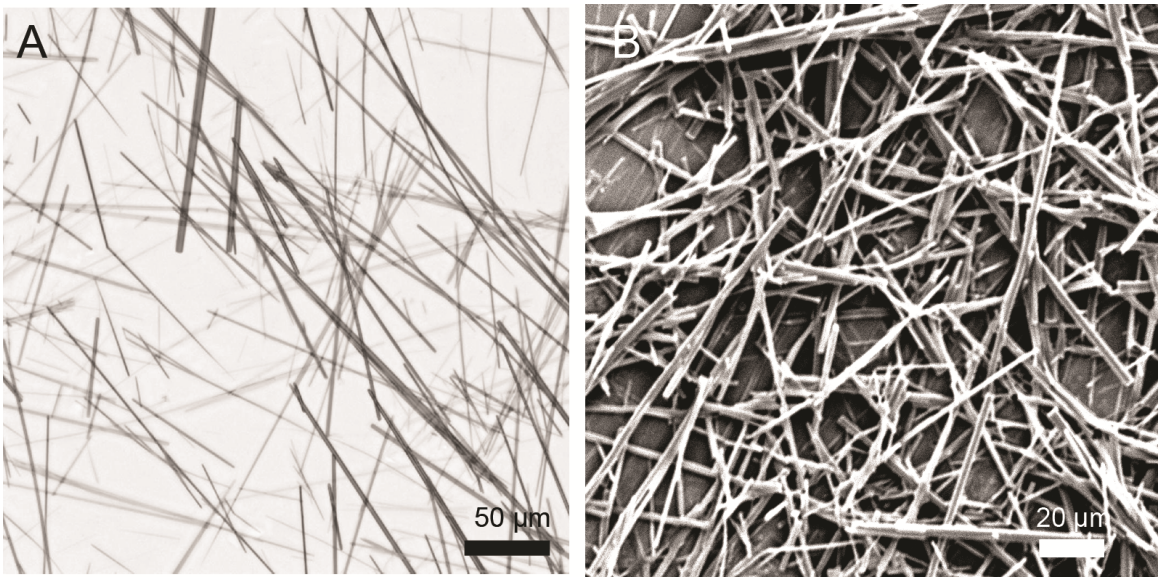


Figure S23. A) OM and B) SEM image of a gel of **3d** formed from purified material (48 mM in EtOH/borax buffer (9/1, v/v)).

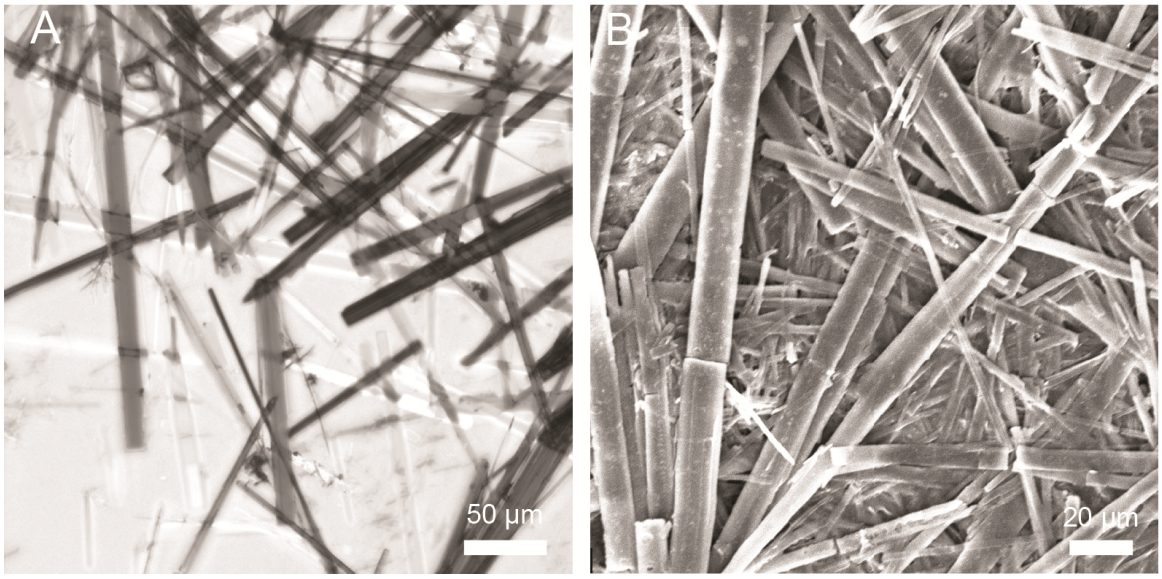


Figure S24. A) OM and B) SEM image of a gel of **3e** formed from purified material (37 mM in EtOH/borax buffer (9/1, v/v)).

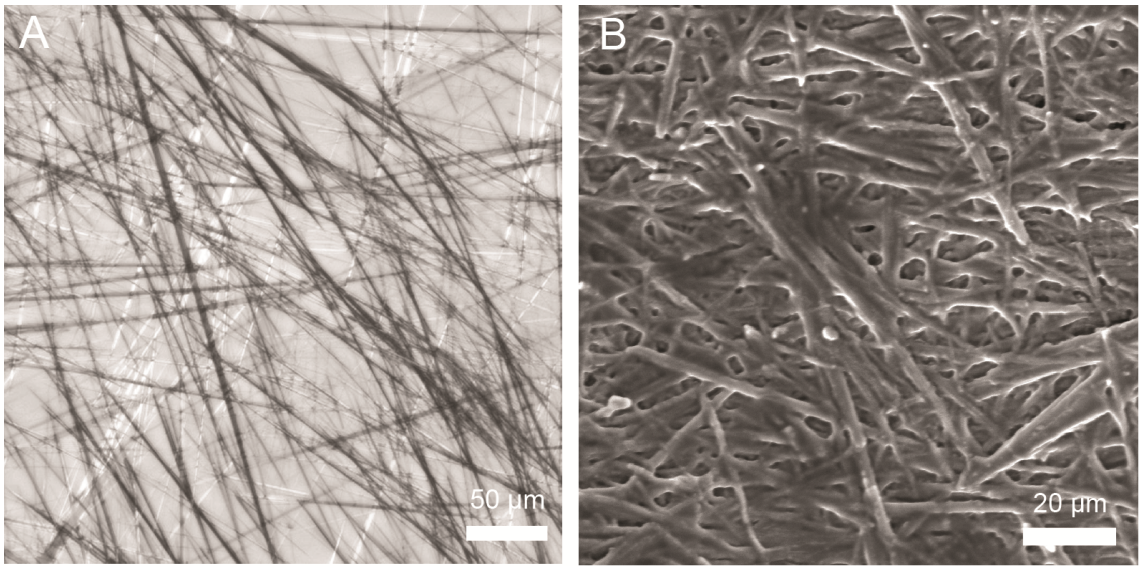


Figure S25. A) OM and B) SEM image of a gel of **3f** formed from purified material (30 mM in borax buffer).

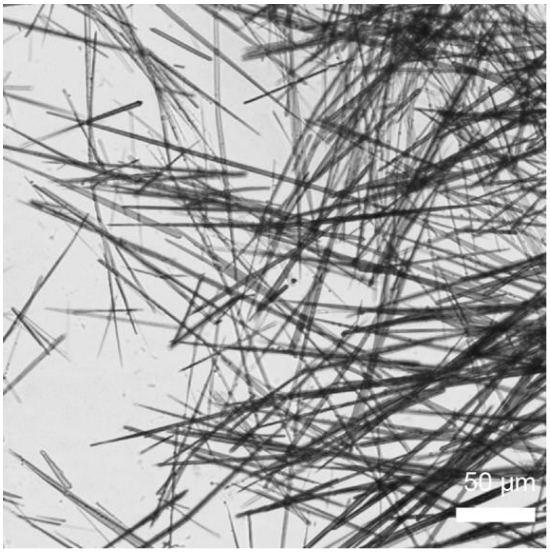
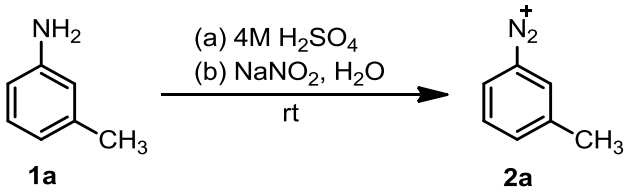


Figure S26. OM image of a gel of **3g** formed from purified material (49 mM in EtOH/borax buffer (9/1, v/v)).

IX. Diazonium Ion Formation by UV-vis and ^{1}H NMR Spectroscopy



1a **2a**

Preparation of stock solutions

Aniline Stock Solution – **1a** (0.025 mL, 0.20 mmol) was dissolved in aq. H_2SO_4 (10 mL, 4 M). Then 0.1 mL of this solution was diluted with aq. H_2SO_4 (0.9 mL, 4 M) to achieve a final concentration of 2.0 mM.

Nitrite Stock Solution - $NaNO_2$ (0.014 g, 0.20 mmol) was dissolved in H_2O (10 mL). Then 0.1 mL of this solution was diluted with H_2O (0.9 mL) to achieve a final concentration of 2.0 mM.

Procedure for forming the diazonium ion - In a 4 mL quartz cuvette, the aniline stock solution (0.1 mL, 2.0 mM) was diluted with aq. H_2SO_4 (3.8 mL, 4 M). The UV-vis spectrum of **1a** was then acquired. To the cuvette, the nitrite stock solution (0.1 mL, 2.0 mM) was added. The cuvette was inverted to mix the solution. Spectra were acquired at various time points over 60 min.

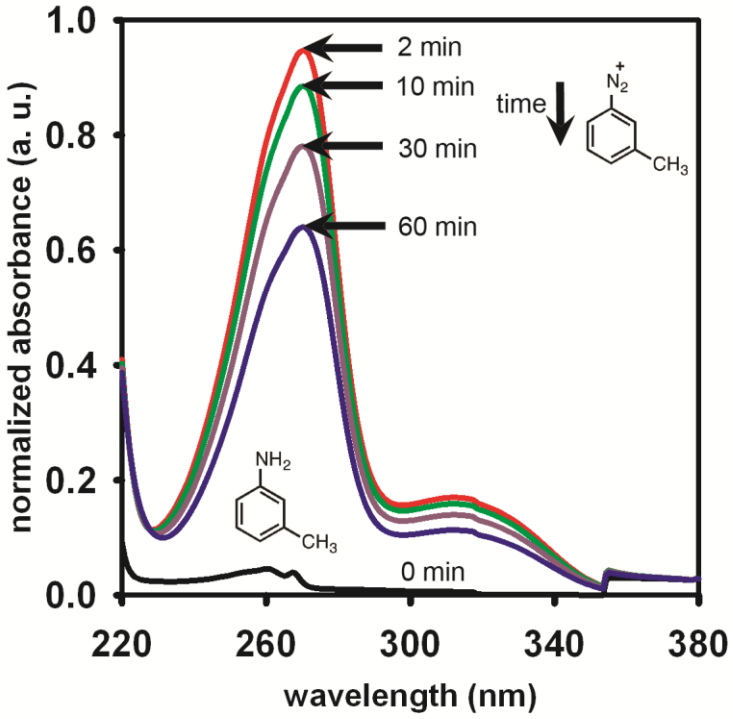
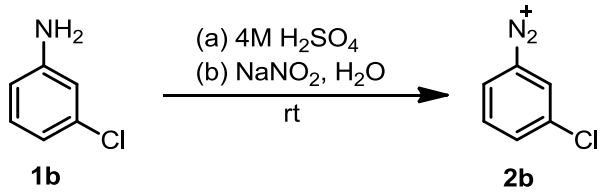


Figure S27. UV-vis spectra of **1a** (λ_{max}, 260.5 nm) to **2a** (λ_{max}, 270.25 nm).



1b **2b**

Preparation of stock solutions

Aniline Stock Solution – **1b** (0.030 mL, 0.28 mmol) was dissolved in aq. H_2SO_4 (10 mL, 4 M). Then 0.1 mL of this solution was diluted with aq. H_2SO_4 (0.9 mL, 4 M) to achieve a final concentration of 2.8 mM.

Nitrite Stock Solution - $NaNO_2$ (0.019 g, 0.28 mmol) was dissolved in H_2O (10 mL). Then 0.1 mL of this solution was diluted with H_2O (0.9 mL) to achieve a final concentration of 2.8 mM

Procedure for forming the diazonium ion - In a 4 mL quartz cuvette, the aniline stock solution (0.3 mL, 2.8 mM) was diluted with aq. H_2SO_4 (3.4 mL, 4 M). The UV-vis spectrum of **1b** was then acquired. To the cuvette, the nitrite stock solution (0.3 mL, 2.8 mM) was added. The cuvette was inverted to mix the solution. Spectra were acquired at various time points over 60 min.

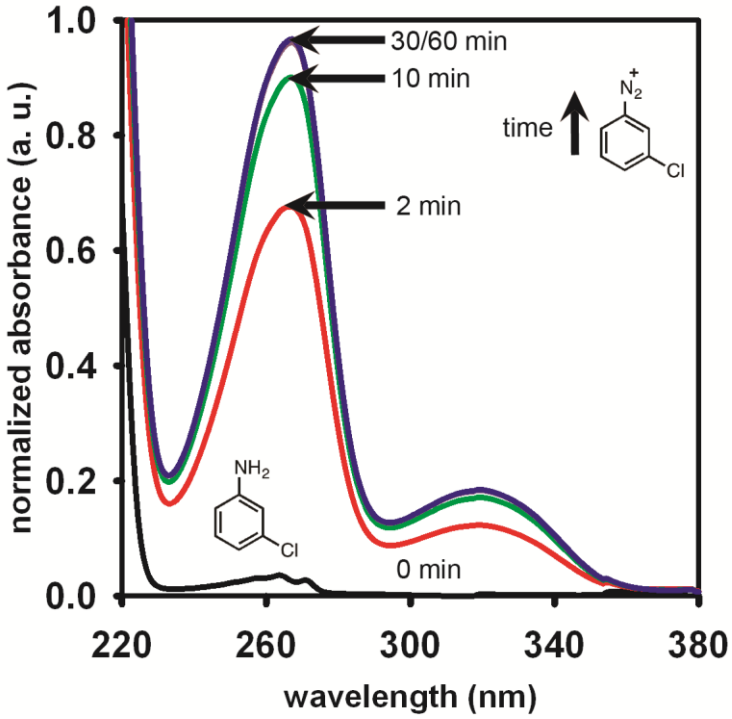
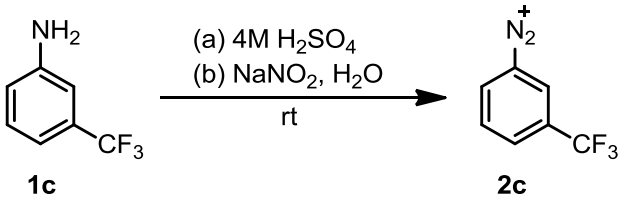


Figure S28. UV-vis spectra of **1b** (λ_{max}, 263.50 nm) to **2b** (λ_{max}, 266.50 nm).



1c **2c**

Preparation of stock solutions

Aniline Stock Solution – **1c** (0.035 mL, 0.28 mmol) was dissolved in aq. H_2SO_4 (10 mL, 4 M). Then 0.1 mL of this solution was diluted with aq. H_2SO_4 (0.9 mL, 4 M) to achieve a final concentration of 2.8 mM.

Nitrite Stock Solution - $NaNO_2$ (0.019 g, 0.28 mmol) was dissolved in H_2O (10 mL). Then 0.1 mL of this solution was diluted with H_2O (0.9 mL) to achieve a final concentration of 2.8 mM.

Procedure for forming the diazonium ion - In a 4 mL quartz cuvette, the aniline stock solution (0.2 mL, 2.8 mM) was diluted with aq. H_2SO_4 (3.6 mL, 4 M). The UV-vis spectrum of **1c** was then acquired. To the cuvette, the nitrite stock solution (0.2 mL, 2.8 mM) was added. The cuvette was inverted to mix the solution. Spectra were acquired at various time points.

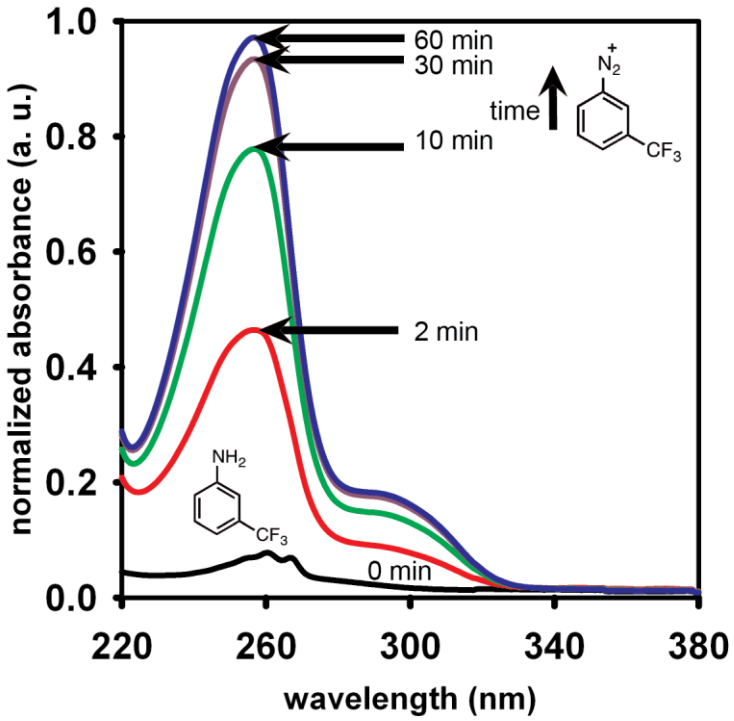
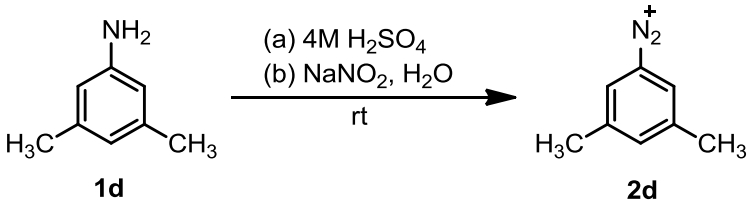


Figure S29. UV-vis spectra of **1c** (λ_{max}, 260 nm) to **2c** (λ_{max}, 256 nm).



1d **2d**

Preparation of Stock Solutions

Aniline Stock Solution – **1d** (0.025 mL, 0.20 mmol) was dissolved in aq. H_2SO_4 (10 mL, 4 M). Then 0.1 mL of this solution was diluted with aq. H_2SO_4 (0.9 mL, 4 M) to achieve a final concentration of 2.0 mM.

Nitrite Stock Solution - $NaNO_2$ (0.014 g, 0.20 mmol) was dissolved in H_2O (10 mL). Then 0.1 mL of this solution was diluted with H_2O (0.9 mL) to achieve a final concentration of 2.0 mM

Procedure for forming the diazonium ion - In a 4 mL quartz cuvette, the aniline stock solution (0.04 mL, 2.0 mM) was diluted with aq. H_2SO_4 (3.92 mL, 4M). The UV-vis spectrum of **1d** was then acquired. To the cuvette, the nitrite stock solution (0.04 mL, 2.0 mM) was added. The cuvette was inverted to mix the solution. Spectra were acquired at various time points over 60 min.

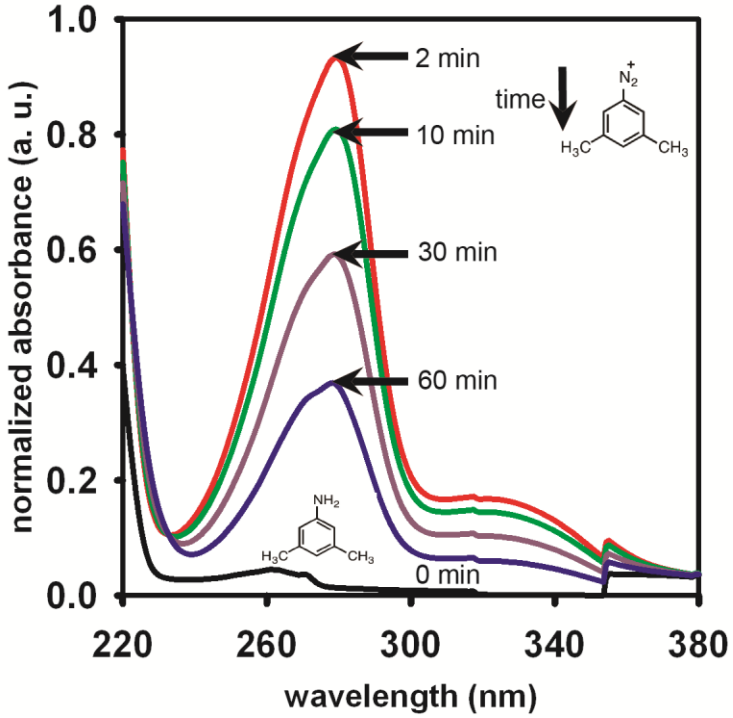
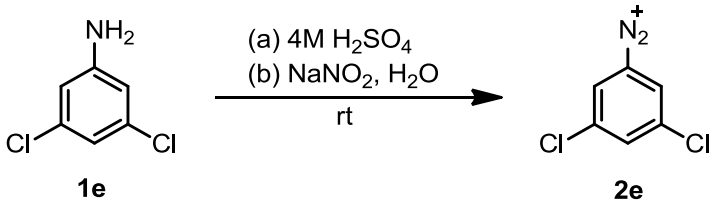


Figure S30. UV-vis spectra of **1d** (λ_{max}, 261.25 nm) to **2d** (λ_{max}, 278.5 nm).



1e **2e**

Preparation of stock solutions

Aniline Stock Solution – **1e** (0.026 g, 0.16 mmol) was dissolved in aq. H_2SO_4 (10 mL, 4 M). Then 0.1 mL of this solution was diluted with aq. H_2SO_4 (0.9 mL, 4 M) to achieve a final concentration of 1.6 mM.

Nitrite Stock Solution - $NaNO_2$ (0.011 g, 0.16 mmol) was dissolved in H_2O (10 mL). Then 0.1 mL of this solution was diluted with H_2O (0.9 mL) to achieve a final concentration of 1.6 mM

Procedure for forming the diazonium ion - In a 4 mL quartz cuvette, the aniline stock solution (0.3 mL, 1.6 mM) was diluted with aq. H_2SO_4 (3.4 mL, 4 M). The UV-vis spectrum of **1e** was then acquired. To the cuvette, the nitrite stock solution (0.3 mL, 1.6 mM) was added. The cuvette was inverted to mix the solution. Spectra were acquired at various time points over 60 min.

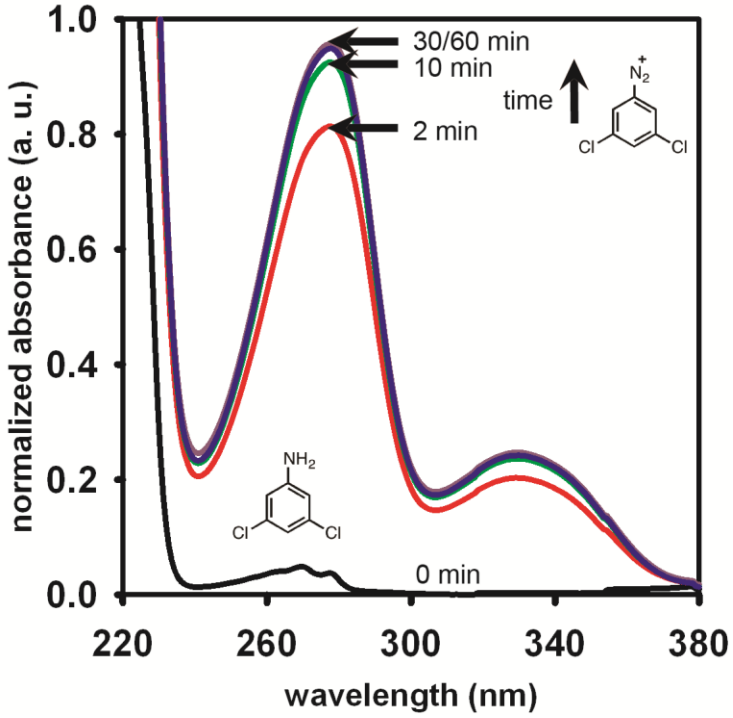
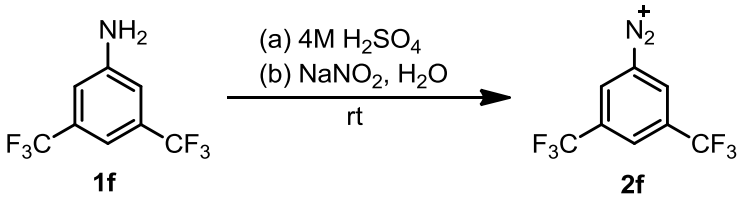


Figure S31. UV-vis spectra of **1e** (λ_{max}, 269.50 nm) to **2e** (λ_{max}, 277.75 nm).



Preparation of stock solutions

Aniline Stock Solution – **1f** (0.040 mL, 0.32 mmol) was dissolved in aq. H_2SO_4 (10 mL, 4 M). Then 0.1 mL of this solution was diluted with aq. H_2SO_4 (0.9 mL, 4 M) to achieve a final concentration of 3.2 mM.

Nitrite Stock Solution - $NaNO_2$ (0.023 g, 0.33 mmol) was dissolved in H_2O (10 mL). Then 0.1 mL of this solution was diluted with H_2O (0.9 mL) to achieve a final concentration of 3.3 mM

Procedure for forming the diazonium ion - In a 4 mL quartz cuvette, the aniline stock solution (0.2 mL, 3.2 mM) was diluted with aq. H_2SO_4 (3.6 mL, 4M). The UV-vis spectrum of **1f** was then acquired. To the cuvette, the nitrite stock solution (0.2 mL, 3.3 mM) was added. The cuvette was inverted to mix the solution. Spectra were acquired at various time points over 60 min.

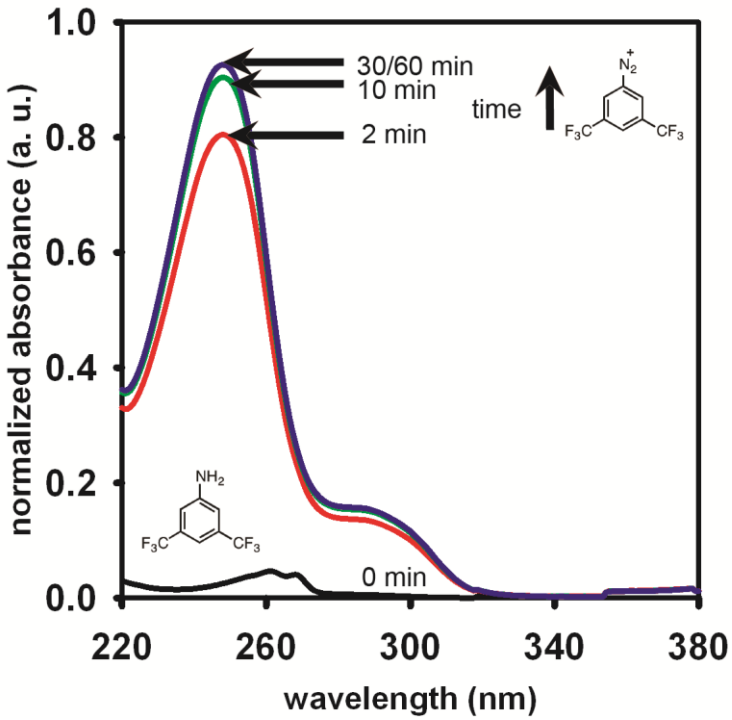
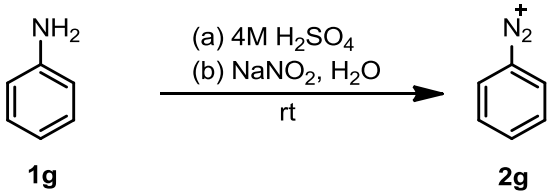


Figure S32. UV-vis spectra of **1f** (λ_{max}, 261.25 nm) to **2f** (λ_{max}, 247.25 nm).



Preparation of stock solutions

Aniline Stock Solution – **1g** (0.018 mL, 0.20 mmol) was dissolved in aq. H_2SO_4 (10 mL, 4 M). Then 0.1 mL of this solution was diluted with aq. H_2SO_4 (0.9 mL, 4 M) to achieve a final concentration of 2.0 mM.

Nitrite Stock Solution - $NaNO_2$ (0.015 g, 0.20 mmol) was dissolved in H_2O (10 mL). Then 0.1 mL of this solution was diluted with H_2O (0.9 mL) to achieve a final concentration of 2.0 mM.

Procedure for forming the diazonium ion - In a 4 mL quartz cuvette, the aniline stock solution (0.06 mL, 2.0 mM) was diluted with aq. H_2SO_4 (3.88 mL, 4 M). The UV-vis spectrum of **1g** was then acquired. To the cuvette, the nitrite stock solution (0.06 mL, 2.0 mM) was added. The cuvette was inverted to mix the solution. Spectra were acquired at various time points over 60 min.

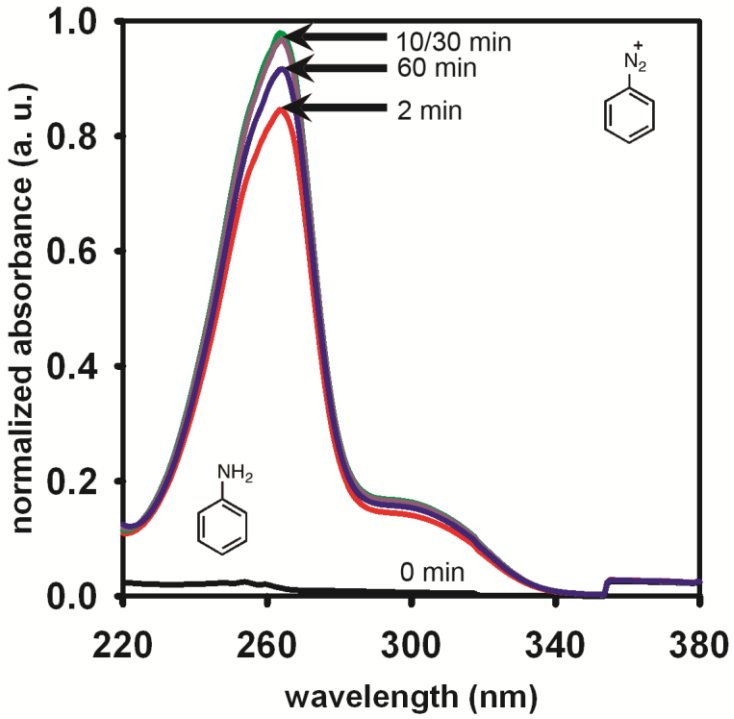


Figure S33. UV-vis spectra of **1g** (λ_{max}, 253.75 nm) to **2g** (λ_{max}, 264.25 nm).

[1]H NMR spectroscopic study of diazonium ion formation

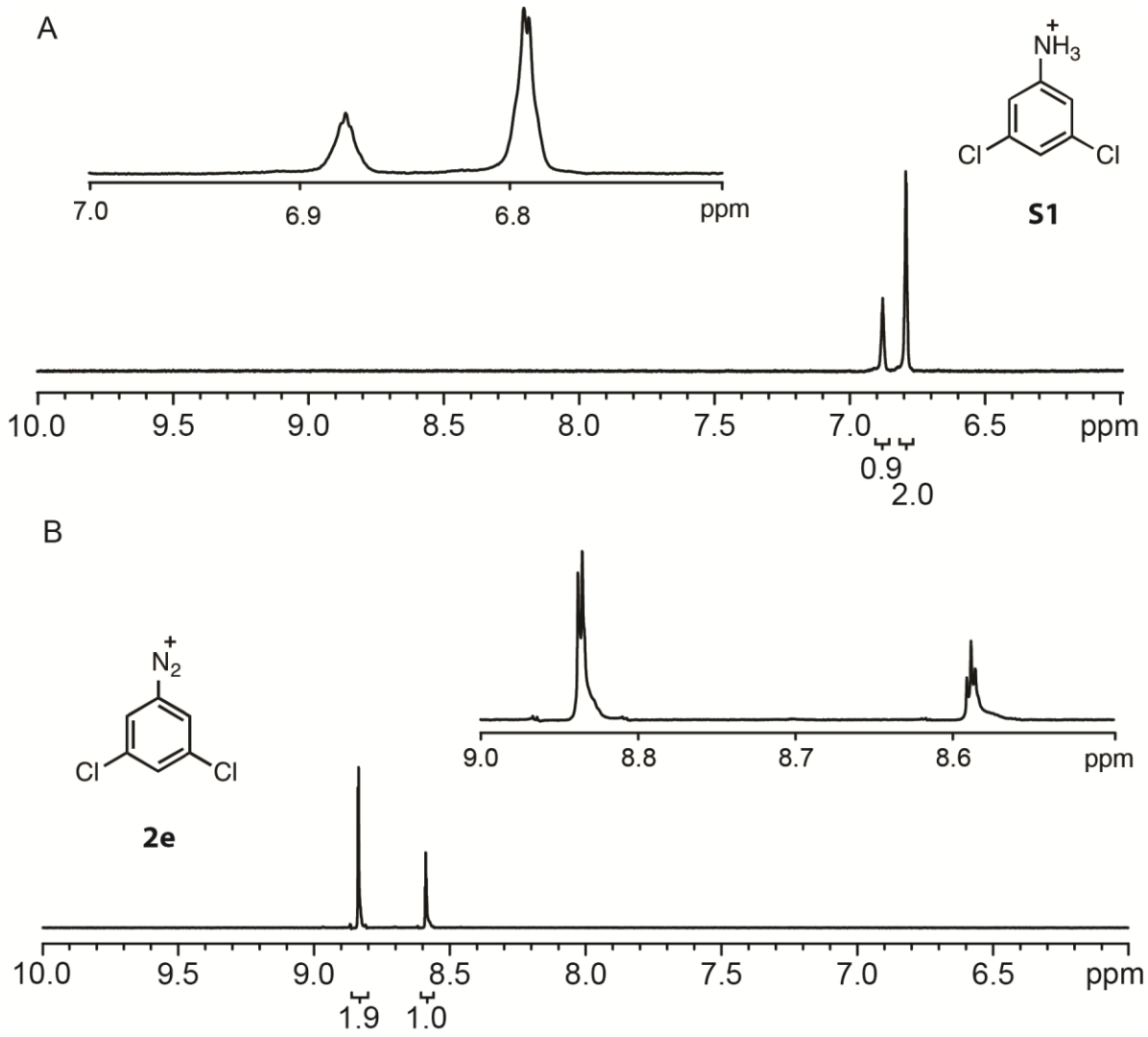
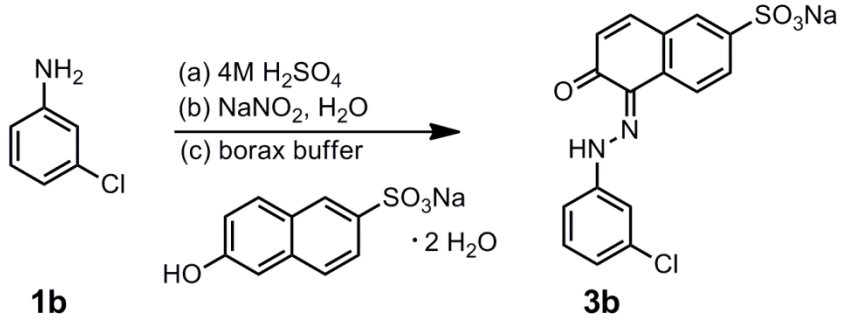


Figure S34. (A) [1]H NMR spectrum of **S1** in H_2SO_4 (4 M). [1]H NMR (700 MHz, DMSO-d_6) δ 6.88 (t, J = 1.8 Hz, 1H), 6.79 (d, J = 1.8 Hz, 2H), (B) [1]H NMR spectrum of **2e** H_2SO_4 (4 M). [1]H NMR (700 MHz, DMSO-d_6) δ 8.84 (d, J = 1.9 Hz, 2H), 8.59 (t, J = 1.9, 1H).

X. Product Formation of 3b, 3c, 3e, and 3f by ^{1}H NMR Spectroscopy



Preparation of stock solutions

D_2O borax buffer (65 mM) – $Na_2B_4O_7.H_2O$ (0.25 g, 5.2 mmol) and NaOH (0.85 g, 170 mmol) were dissolved in D_2O (10 mL).

D_2O H_2SO_4 (4 M) – H_2SO_4 (2.0 mL, 18 M) was added to D_2O (7.2 mL).

Sodium nitrite stock solution (175 mM) – In a 4 mL vial, $NaNO_2$ (11.9 mg, 0.172 mmol) was dissolved in D_2O (0.99 mL).

DMSO Stock (704 mM) – DMSO (0.05 mL) was added to D_2O borax buffer (0.95 mL).

Sodium 2-naphthol-6-sulfonate dihydrate/DMSO stock solution (10 mM) – In a 20 mL vial, sodium 2-naphthol-6-sulfonate dihydrate (22.7 mg, 0.0804 mmol) was dissolved in D_2O borax buffer (7.9 mL, 65 mM). To this, DMSO stock was added (0.1 mL, 704 mM) for use as an internal standard.

*Procedure to determine in situ formation of **3b*** – In a 4 mL vial, **1b** (8.1 µL, 0.077 mmol) was dissolved in D_2O H_2SO_4 (2.0 mL, 4 M). To the solution, sodium nitrite (0.4 mL, 175 mM) was added. Then, an aliquot of this reaction mixture (0.24 mL) was taken at 2, 10, 30 and 60 min and reacted with the sodium 2-naphthol-6-sulfonate dihydrate/DMSO (0.76 mL, 10 mM). After 2 min, D_2O borax buffer (0.3 mL, 65 mM) was added to completely dissolve all starting material and product. Each vial contained $NaNO_2$ (0.0070 mmol, 1.0 equiv), sodium 2-naphthol-6-sulfonate dihydrate (0.0077 mmol, 1.1 equiv), and **1b** (0.0077 mmol, 1.1 equiv). All samples were analyzed by ^{1}H NMR spectroscopy for percent yield calculations.

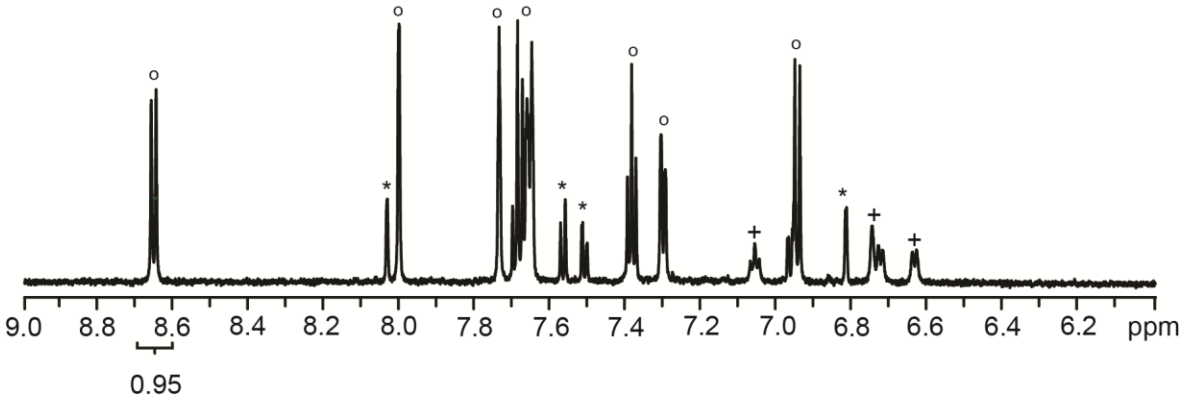
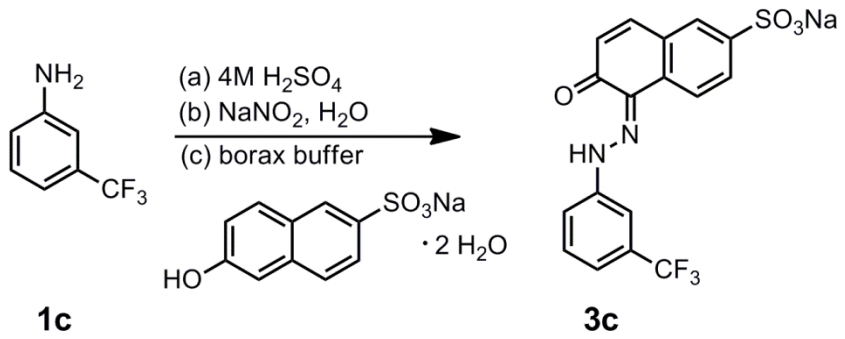


Figure S35. ^{1}H NMR (700 MHz, D_2O) spectrum of **3b** (^{O}) at 60 min. DMSO δ 2.61 (s, 6H). Unreacted sodium 2-naphthol-6-sulfonate dihydrate (*) and **1b** ($^{+}$) are indicated. The peak integrated was used for calculation of the percent yield.

Table S3. Percent yield of **3b** at different time points.

Time (min)	**3b** (mmol)[a]	Yield (%)[b]
2	0.0064	91 ± 1
10	0.0063	90 ± 2
30	0.0065	92 ± 2
60	0.0063	90 ± 1

[a] determined using an internal standard (DMSO)
[b] Percent yield is based on $NaNO_2$ (0.007 mmol). Standard deviation was determined by an average of 2 runs.



1c **3c**

Preparation of stock solutions

D_2O borax buffer (65 mM) – $Na_2B_4O_7.H_2O$ (0.25 g, 5.2 mmol) and NaOH (0.85 g, 170 mmol) were dissolved in D_2O (10 mL).

D_2O H_2SO_4 (4 M) – H_2SO_4 (2.0 mL, 18 M) was added to D_2O (7.2 mL).

Sodium nitrite stock solution (175 mM) – In a 4 mL vial, $NaNO_2$ (11.2 mg, 0.163 mmol) was dissolved in D_2O (0.93 mL).

DMSO Stock (704 mM) – DMSO (0.10 mL) was added to D_2O borax buffer (1.90 mL).

Sodium 2-naphthol-6-sulfonate dihydrate/DMSO stock solution (10 mM) – In a 20 mL vial, sodium 2-naphthol-6-sulfonate dihydrate (21.7 mg, 0.0768 mmol) was dissolved in D_2O borax buffer (7.5 mL, 65 mM). To this, DMSO stock was added (0.1 mL, 704 mM) for use as an internal standard.

*Procedure to determine in situ formation of **3c*** – In a 4 mL vial, **1c** (9.6 µL, 0.077 mmol) was dissolved in D_2O H_2SO_4 (2.0 mL, 4 M). To the solution, sodium nitrite (0.4 mL, 175 mM) was added. Then, an aliquot of this reaction mixture (0.24 mL) was taken at 2, 10, 30 and 60 min and reacted with the sodium 2-naphthol-6-sulfonate dihydrate/DMSO (0.76 mL, 10 mM). After 2 min, D_2O borax buffer (0.3 mL, 65 mM) was added to completely dissolve all starting material and product. Each vial contained $NaNO_2$ (0.0070 mmol, 1.0 equiv), sodium 2-naphthol-6-sulfonate dihydrate (0.0077 mmol, 1.1 equiv), and **1c** (0.0077 mmol, 1.1 equiv). All samples were analyzed by ^1H NMR spectroscopy for percent yield calculations.

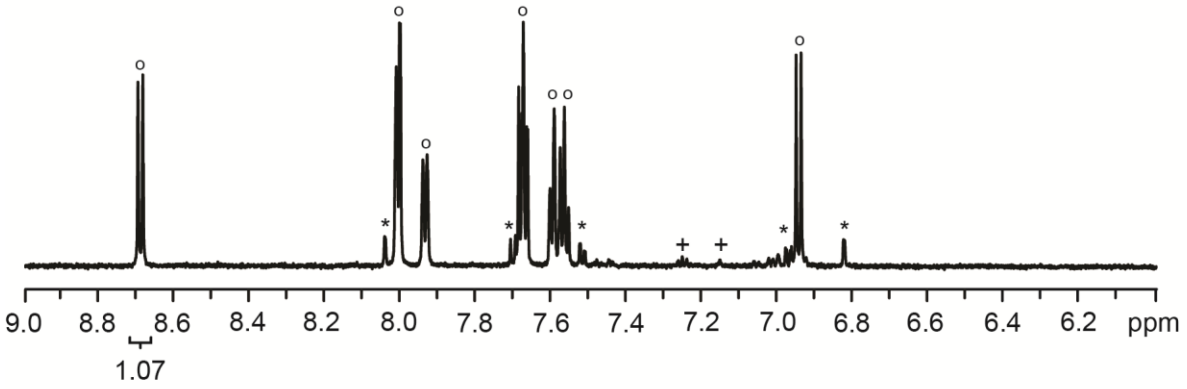


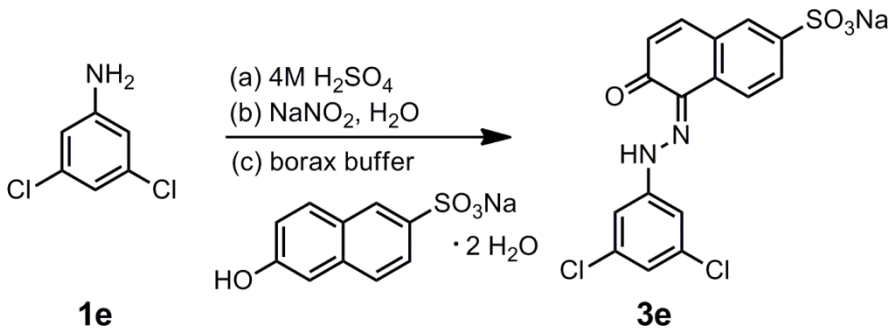
Figure S36. ^{1}H NMR (700 MHz, D_2O) spectrum of **3c** (^{O}) at 60 min. DMSO δ 2.62 (s, 6H). Unreacted sodium 2-naphthol-6-sulfonate dihydrate (*) and **1c** ($^{+}$) are indicated. The peak integrated was used for calculation of the percent yield.

Table S4. Percent yield of **3c** at different time points.

Time (min)	**3c** (mmol)[a]	Yield (%)[b]
2	0.0075	107 ± 2
10	0.0075	107 ± 2
30	0.0077	110 ± 2
60	0.0077	107 ± 2

[a] determined using an internal standard (DMSO)

[b] The relative integrations apparently overestimate the product formation. We believe this overestimation is due to the low concentrations needed to ensure complete solubility of all material. Percent yield is based on $NaNO_2$ (0.007 mmol). Standard deviation was determined by an average of 2 runs.



1e **3e**

Preparation of stock solutions

D_2O borax buffer (65 mM) – $Na_2B_4O_7.H_2O$ (0.25 g, 5.2 mmol) and NaOH (0.85 g, 170 mmol) were dissolved in D_2O (10 mL).

D_2O H_2SO_4 (4 M) – H_2SO_4 (2.0 mL, 18 M) was added to D_2O (7.2 mL).

Sodium nitrite stock solution (175 mM) – In a 4 mL vial, $NaNO_2$ (5.84 mg, 0.0847 mmol) was dissolved in D_2O (0.48 mL).

DMSO Stock (704 mM) – DMSO (0.05 mL) was added to D_2O borax buffer (0.95 mL).

Sodium 2-naphthol-6-sulfonate dihydrate/DMSO stock solution (10 mM) – In a 20 mL vial, sodium 2-naphthol-6-sulfonate dihydrate (11.5 mg, 0.0409 mmol) was dissolved in D_2O borax buffer (3.9 mL, 65 mM). To this, DMSO stock was added (0.1 mL, 704 mM) for use as an internal standard.

*Procedure to determine in situ formation of **3e*** – In a 4 mL vial, **1e** (12.6 mg, 0.0772 mmol) was dissolved in D_2O H_2SO_4 (2.0 mL, 4 M). To the solution, sodium nitrite (0.4 mL, 175 mM) was added. Then, an aliquot of this reaction mixture (0.24 mL) was taken at 2, 10, 30 and 60 min and reacted with the sodium 2-naphthol-6-sulfonate dihydrate/DMSO (0.76 mL, 10 mM). After 2 min, D_2O borax buffer (3.0 mL, 65 mM) was added to completely dissolve all starting material and product. Then an aliquot of the mixture (0.1 mL) was added to an NMR tube and diluted with D_2O (0.5 mL). Each vial contained $NaNO_2$ (0.0071 mmol, 1.0 equiv), sodium 2-naphthol-6-sulfonate dihydrate (0.0078 mmol, 1.1 equiv), and **1e** (0.0078 mmol, 1.1 equiv). All samples were analyzed by ^1H NMR spectroscopy for percent yield calculations.

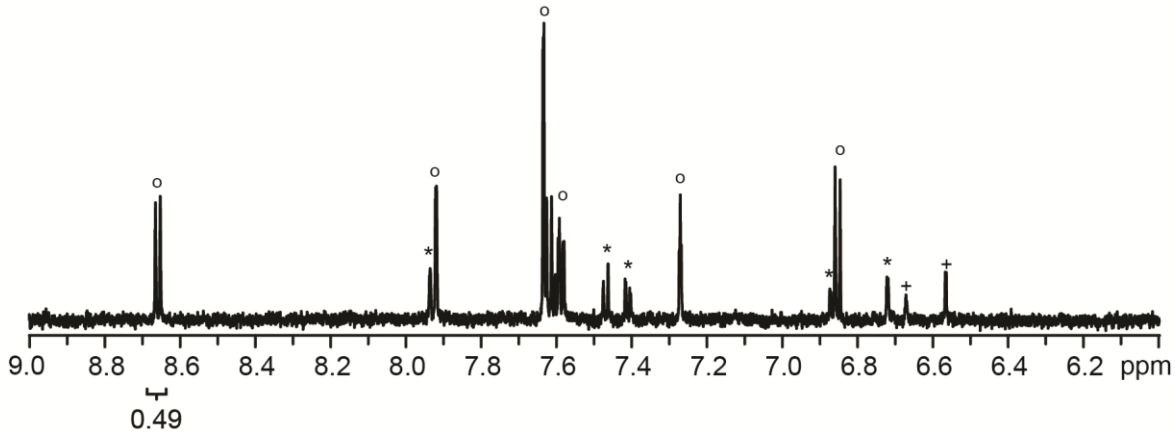
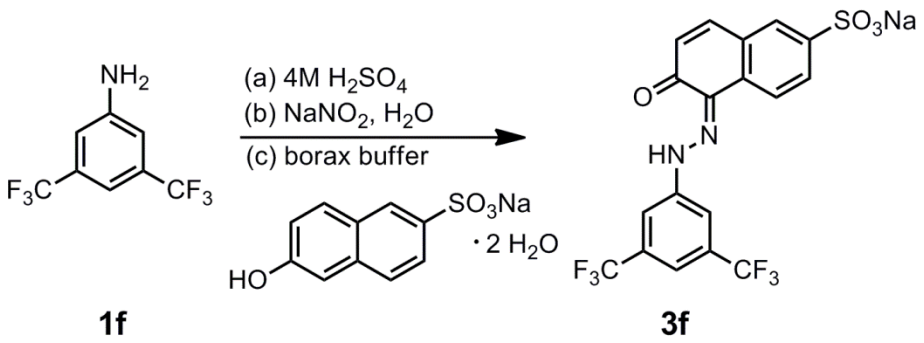


Figure S37. ^{1}H NMR (700 MHz, D_2O) spectrum of **3e** (^{O}) at 60 min. DMSO δ 2.52 (s, 6H). Unreacted sodium 2-naphthol-6-sulfonate dihydrate (*) and **1e** ($^{+}$) are indicated. The peak integrated was used for calculation of the percent yield.

Table S5. Percent yield of **3e** at different time points.

Time (min)	**3e** (mmol)[a]	Yield (%)[b]
2	0.0058	82 ± 1
10	0.0063	89 ± 3
30	0.0063	89 ± 9
60	0.0066	93 ± 8

[a] determined using an internal standard (DMSO)
[b] Percent yield is based on $NaNO_2$ (0.0071 mmol). Standard deviation was determined by an average of 2 runs.



1f **3f**

Preparation of stock solutions

D_2O borax buffer (65 mM) – $Na_2B_4O_7.H_2O$ (5.2 mmol) and NaOH (170 mmol) were dissolved in D_2O (10 mL).

D_2O H_2SO_4 (4 M) – H_2SO_4 (2.0 mL, 18 M) was added to D_2O (7.2 mL).

Sodium nitrite stock solution (175 mM) – In a 4 mL vial, $NaNO_2$ (11.235 mg, 0.163 mmol) was dissolved in D_2O (0.93 mL).

DMSO Stock (704 mM) – DMSO (0.10 mL) was added to D_2O borax buffer (1.90 mL).

Sodium 2-naphthol-6-sulfonate dihydrate/DMSO stock solution (10 mM) – In a 20 mL vial, sodium 2-naphthol-6-sulfonate dihydrate (21.7 mg, 0.0768 mmol) was dissolved in D_2O borax buffer (7.5 mL, 65 mM). To this, DMSO stock was added (0.10 mL, 704 mM) for use as an internal standard.

*Procedure to determine in situ formation of **3f*** – In a 4 mL vial, **1f** (12 µL, 0.077 mmol) was dissolved in D_2O H_2SO_4 (2.0 mL, 4 M). To the solution, sodium nitrite (0.4 mL, 175 mM) was added. Then, an aliquot of this reaction mixture (0.24 mL) was taken at 2, 10, 30 and 60 min and reacted with the sodium 2-naphthol-6-sulfonate dihydrate/DMSO (0.76 mL, 10 mM). After 2 min, D_2O borax buffer (0.3 mL, 65 mM) was added to completely dissolve all starting material and product. Each vial contained $NaNO_2$ (0.0070 mmol, 1.0 equiv), sodium 2-naphthol-6-sulfonate dihydrate (0.0077 mmol, 1.1 equiv), and **1f** (0.0077 mmol, 1.1 equiv). All samples was analyzed by ^1H NMR spectroscopy for percent yield calculations.

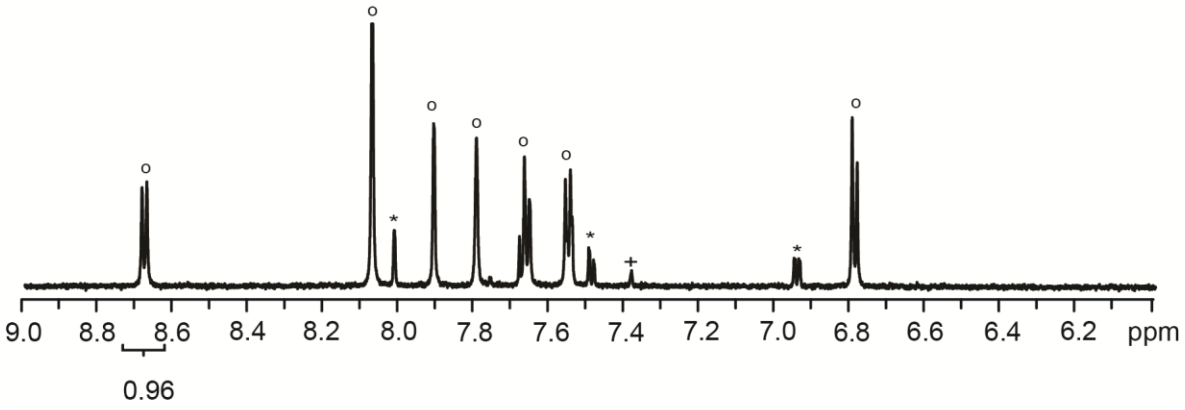


Figure S38. ^{1}H NMR (700 MHz, D_2O) spectra of **3f** (^{O}) at 60 min. DMSO δ 2.60 (s, 6H). Unreacted sodium 2-naphthol-6-sulfonate dihydrate (*) and **1f** ($^{+}$) are indicated. The peak integrated was used for calculation of the percent yield.

Table S6. Percent yield of **3f** at different time points.

Time (min)	**3f** (mmol)[a]	Yield (%)[b]
2	0.0070	100 ± 1
10	0.0068	97 ± 2
30	0.0068	97 ± 3
60	0.0068	97 ± 3

[a] determined using an internal standard (DMSO)
[b] Percent yield is based on $NaNO_2$ (0.007 mmol). Standard deviation was determined by an average of 2 runs.

[1]H NMR spectroscopic study of **3e** formation in situ

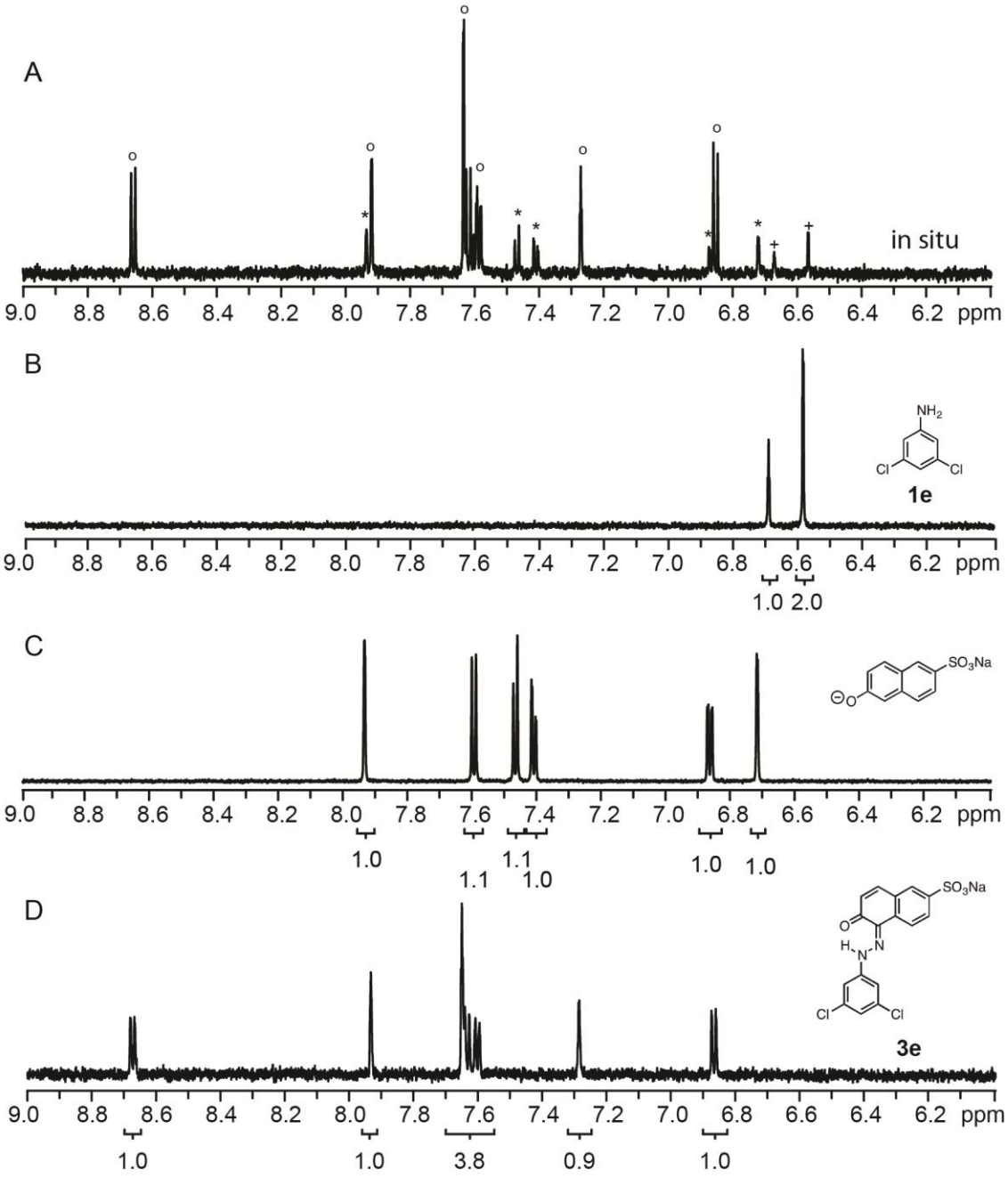


Figure S39. [1]H NMR spectra of (A) **3e** in in situ conditions (700 MHz, D_2O borax buffer) where [+]**1e**, *sodium 2-naphthol-6-sulfonate dehydrate, and [o]**3e**. (B) **1e** (700 MHz, D_2O borax buffer) δ 6.90 (t, *J* = 1.7 Hz, 1H), 6.58 (d, *J* = 1.7 Hz, 2H), (C) sodium 2-naphthol-6-sulfonate dihydrate (700 MHz, D_2O borax buffer) δ 7.93 (s, 1H), 7.60 (d, *J* = 9.1 Hz, 1H) 7.47 (d, *J* = 8.6 Hz, 1H), 7.42 (dd, *J* = 8.8, 1.7 Hz, 1H) 6.87 (dd, *J* = 9.3, 2.8 Hz, 1H), 6.72 (d, *J* = 2.3 Hz, 1H). (D) **3e** (700 MHz, D_2O borax buffer) δ 8.68 (d, *J* = 9.0 Hz, 1H), 7.93 (s, 1H) 7.65 (m, 4H), 7.29 (d, *J* = 2.08 Hz, 1H), 6.88 (d, *J* = 9.4 Hz, 1H).

XI. In Situ Gelation and In Situ Gelation in Environmental Conditions

In situ detection of NO_2^- in a 4 mL vial

Preparation of stock solutions

1e *solution (62.0 mM)* – **1e** (21.1 mg, 0.130 mmol) was dissolved in H_2SO_4 (2.1 mL, 4 M).

Sodium nitrite solution (276 mM) – $NaNO_2$ (32.4 mg, 0.470 mmol) was dissolved in H_2O (1.7 mL).

Sodium 2-naphthol-6-sulfonate dihydrate (16.2 mM) – Sodium 2-naphthol-6-sulfonate dihydrate (34.7 mg, 0.123 mmol) was dissolved in borax buffer (7.6 mL, 65 mM).

Representative procedure for in situ detection of NO_2^- - In a 4 mL vial, $NaNO_2$ solution (40 µL, 276 mM) was reacted with the **1e** solution (0.2 mL, 62.0 mM). The vial was shaken for 30 s and let stand to react for 10 min. Then the sodium 2-naphthol-6-sulfonate dihydrate solution (0.76 mL, 16.2 mM) was added and a color change from slight yellow to red-orange was observed. The vial was heated with a heat gun until all compounds were dissolved and then allowed to cool to rt.

Table S7. Concentration of NO_2^-

In Situ Generated Gelator	$NaNO_2$ (mmol)	Final NO_2^- (ppm)
3b	0.033	1500
3c	0.028	1300
3e	0.011	500

In situ detection of NO_2^- in a 1.5 mL vial

Preparation of stock solutions

***1e** solution (11.0 mM)* – **1e** (5.53 mg, 0.0341 mmol) was dissolved in H_2SO_4 (3.1 mL, 4 M).

Sodium nitrite solution (49.0 mM) – $NaNO_2$ (3.08 mg, 0.0446 mmol) was dissolved in H_2O (0.91 mL).

Sodium 2-naphthol-6-sulfonate dihydrate (2.87 mM) – Sodium 2-naphthol-6-sulfonate dihydrate (3.23 mg, 0.0115 mmol) was dissolved in borax buffer (4.0 mL, 65 mM).

Procedure for in situ detection of NO_2^- - In a 1.5 mL vial, $NaNO_2$ solution (20 µL, 49.0 mM) was reacted with the **1e** solution (0.1 mL, 11.0 mM). The vial was shaken for 30 s and let stand to react for 10 min. Then sodium 2-naphthol-6-sulfonate dihydrate solution (0.38 mL, 2.87 mM) was added and a color change from slight yellow to red-orange was observed. The vial was shaken for 5 s, sonicated for 10 s and then allowed to stand at rt for 5 min.

Table S8. Concentration of NO_2^-

In Situ Generated Gelator	$NaNO_2$ (mmol)	Final NO_2^- (ppm)
3e	0.00098	90

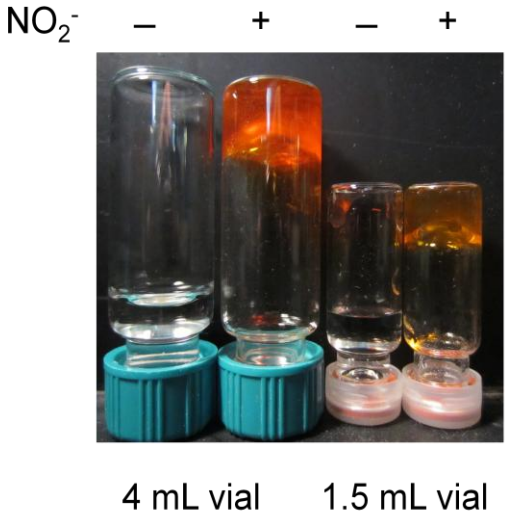


Figure S40. In situ gels of **3e** at 500 ppm of NO_2^- in a 4 mL vial and 90 ppm of NO_2^- in a 1.5 mL vial with negative controls.

Gelation in environmental conditions procedure – In situ gels of **3e** were formed via the representative procedure for in situ detection for NO_2^- (pg. S43). However, water from four different sources (lab tap water, Huron River water, pond water and muddy pond water) were spiked with $NaNO_2$ (0.76 mg, 0.011 mmol) and used in place of the sodium nitrite stock solution to determine if gelation occurred in environmental conditions. Additionally, a negative control with no $NaNO_2$ added was performed for each water source. Results are shown in Figure S38.

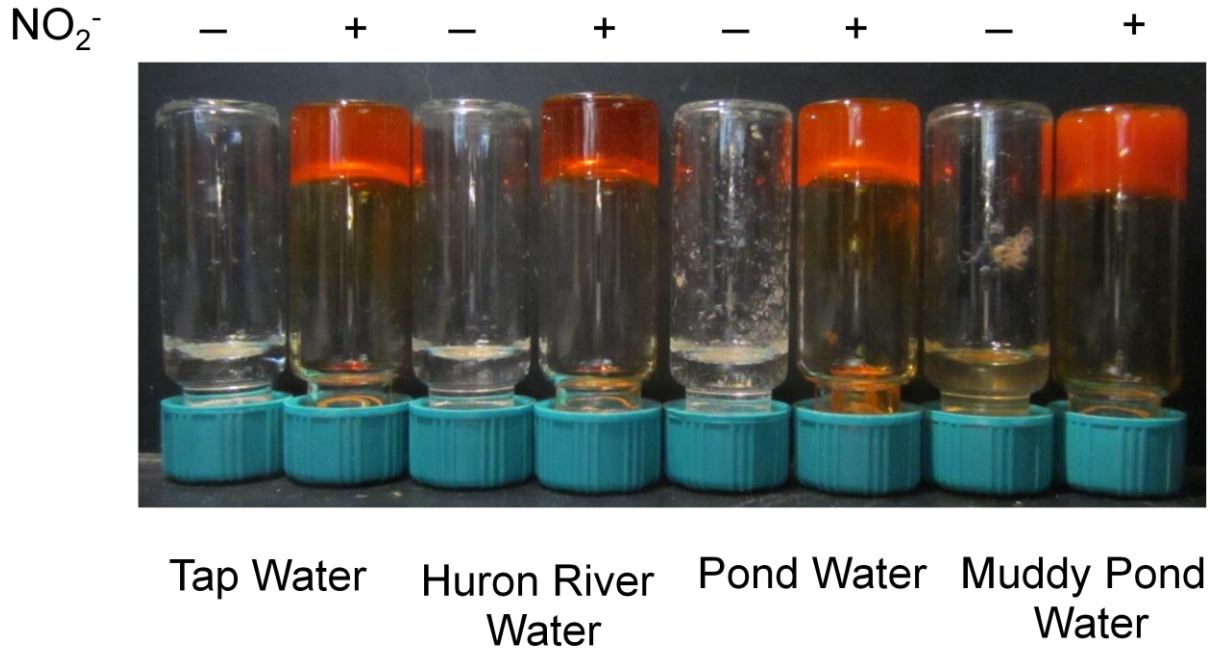


Figure S41. In situ gels of **3e** at 500 ppm of NO_2^- in various sources.

In situ detection of NO_2^- from a NO_2^- standard in a 1.5 mL vial

Preparation of stock solutions

1e *solution (12.1 mM)* – **1e** (1.94 mg, 0.0120 mmol) was dissolved in H_2SO_4 (0.99 mL, 4 M).

Sodium 2-naphthol-6-sulfonate dihydrate (2.95 mM) – Sodium 2-naphthol-6-sulfonate dihydrate (3.06 mg, 0.0109 mmol) was dissolved in borax buffer (3.65 mL, 65 mM).

Procedure for in situ detection of NO_2^- - In a 1.5 mL vial, SPEX Certiprep nitrite-nitrogen standard (45 µL, 1000 ppm) was reacted with the **1e** solution (0.09 mL, 12.1 mM). The vial was shaken for 30 s and let stand to react for 10 min. Then sodium 2-naphthol-6-sulfonate dihydrate solution (0.365 mL, 2.95 mM) was added and a color change from slight yellow to red-orange was observed. The vial was shaken for 5 s, sonicated for 5 s and then allowed to stand at rt for 10 min.

Table S8. Concentration of NO_2^-

In Situ Generated Gelator	Final NO_2^- (ppm)
3e	90

XI. Reference

1. Kalatzis, E. *J. Chem. Soc. B.* **1967**, 273-277.