Supplementary Information

Sugar Isoxazole Based Hydrogelators and Their Applications as Reusable Hydrogels for Dye Removal

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Experimental Section

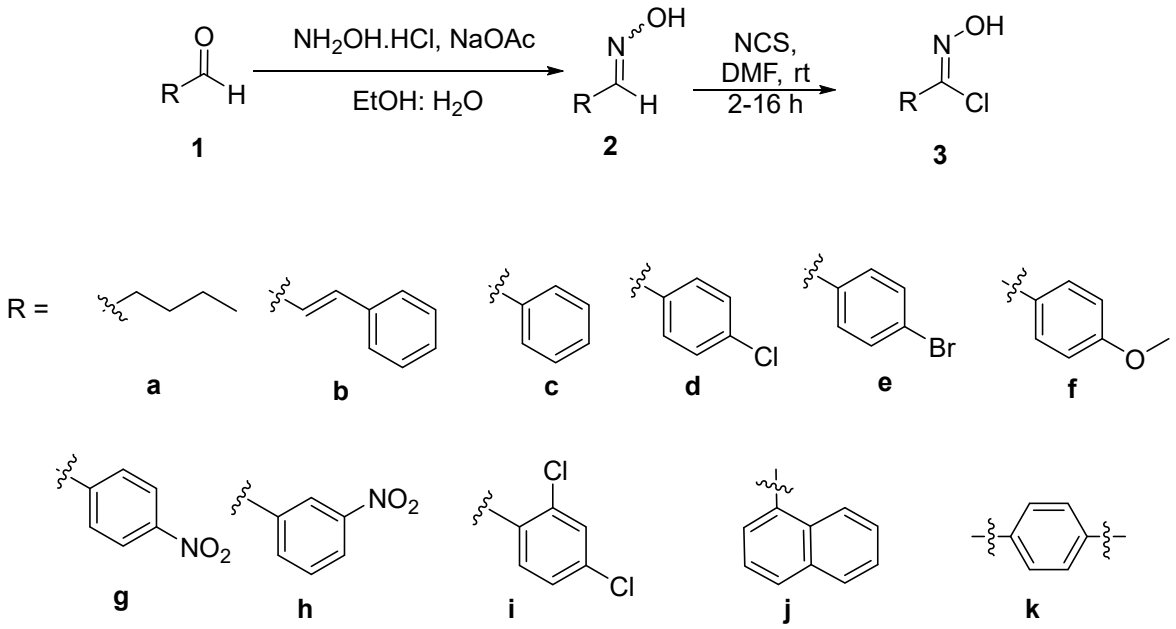
General Methods

All reactions unless otherwise noted were carried out in oven dried glassware under nitrogen atmosphere. Reagents and solvents were purchased from commercial suppliers from Sigma-Aldrich, VWR, Fisher, etc. and used directly without purifications. Purification was mostly conducted by flash chromatography using 230-400 mesh silica gel with a gradient of solvent systems, and sometimes recrystallization. Thin-layer chromatography (TLC) analysis was performed with aluminum backed TLC plates (Sigma-Aldrich) with UV and fluorescence indicator and visualized using UV lamp at 254 nm then stained with PMA solution. ^{1}H and proton-decoupled ^{13}C NMR spectra were obtained with Bruker 400 MHz spectrometers in DMSO-d_6 or $CDCl_3$. The chemical shifts used $CDCl_3$/DMSO-d_6 as internal standards at 7.26/2.50 ppm and at 77.0/39.5 ppm, respectively. Some 2D NMR experiments (HSQC, COSY) were also conducted to assist the NMR assignment. Melting point measurements were carried out using a Fisher Jones melting point apparatus. High Resolution mass spectra (HRMS) were obtained on a Thermo Scientific LTQ Discovery spectrometer using +ESI and reported for the molecular ion $[M+Na]^+$.

I. Synthesis of chloro-oxime intermediates

The syntheses of different chloro-oxime intermediates are provided in Scheme S1, these compounds were synthesized from the corresponding aldehyde **1 (a-k)** by converting them to hydroxyl amines **2** and followed by treatment with NCS to form the chloro-oximes **3 (a-k)**, these chloro-oximes have been reported previously and our NMR data and spectra match the literature reports.[1,2] The preparation procedure and NMR spectra are included in the SI. The synthesis of isoxazoles followed methods reported in the literature with certain modification.[3,4] The following section gives the general method for their synthesis, the detailed preparation procedures of the first

two compounds are included. The ^{1}H NMR spectra and some ^{13}C NMR spectra for these intermediates are provided.



Scheme S1. Structures of the chloro-oximes synthesized.

Synthesis of compound **3a**

The hydroxyl amine **2a** was prepared first. To a 100 mL round bottomed flask (RBF) with a condenser, valeraldehyde **1a** (1.0 g, 11.6 mmol, 1.0 equiv), $NH_2OH{\cdot}HCl$ (1.21 g, 17.4 mmol, 1.5 equiv), and NaOAc (2.38 g, 29.02 mmol, 2.5 equiv) in ethanol (6.0 mL) and water (12.0 mL) were added. The reaction mixture was stirred heated to 95 ^{o}C under refluxing conditions and the reaction progress was monitored by ^{1}H NMR. After 2.0 h, the ^{1}H NMR indicates reaction completion. The reaction was stopped, and ethanol was removed on a rotavap. The residue was worked up by adding dichloromethane (DCM) and the product was extracted using a separatory funnel. The organic layer was dried over anhydrous Na_2SO_4, then filtered and the solvent was removed on a rotavap to obtain the hydroxylamine **2a** as a white solid. ^{1}H NMR spectrum shows the presence of both E

and Z isomers. This was used directly for the next step. Compound **2a** (0.8 g, 7.9 mmol, 1.0 equiv) was dissolved in anhydrous DMF (3.0 mL) in a 50 mL round bottomed flask. To this stirring solution, *N*-chloro succinimide (NCS) (1.0 g, 7.9 mmol, 1.0 equiv) dissolved in 5.0 mL of anhydrous DMF was added dropwise over a period of 1.0 h. The reaction was stirred at rt for an addition 5.0 h, at which time ^{1}H NMR sample showed full conversion of the starting material. The reaction was stopped, and the solvent was removed used a rotavap under reduced pressure, the residue was diluted with EtOAc (25 mL) then washed with water (2 X 10 mL). The organic layer was then dried over Na_2SO_4, filtered and the solvent was removed using a rotavap to afford the crude product as an off-white liquid. The crude was further purified using column chromatography (Hexanes to 1% EtOAc) to obtain the product **3a** as a colorless oil in 77 % yield (825 mg), R_f = 0.47 (5% EtOAc/Hexanes).

Synthesis of compound **3b**

A mixture of cinnamaldehyde (1.0 g, 5.40 mmol, 1.0 equiv), $NH_2OH{\cdot}HCl$ (563.37 mg, 8.10 mmol, 1.5 equiv), and NaOAc (1.1 g, 13.5 mmol, 2.5 equiv) in ethanol (6.0 mL) and water (12.0 mL) was placed into a 100 mL round-bottomed flask with a reflux condenser. Then the reaction flask was heated to 95 ºC and the reaction progress was monitored by ^{1}H NMR (at 2.0 h point), to see the disappearance of starting material. The reaction was stopped, EtOH was dried under a vacuum, DCM was added to the cloudy water solution, and the compound was extracted using a separatory funnel. The organic layer was dried over anh. Na_2SO_4, filtered and the solvent was removed using a rotavap under vacuum to obtain a brownish viscous liquid as the crude product hydroxyl amine **2b**, which was taken directly to the next step. Compound **2b** (600 mg, 4.07 mmol, 1.0 equiv) was dissolved in DMF (3.0 mL) in a 50 mL round bottomed flask with a stirring bar, NCS (544.4 mg,

4.07 mmol. 1.0 equiv) dissolved in 5.0 mL of DMF was added dropwise to the mixture over a period of 1.0 h. The reaction was stirred at rt for 24 h, ^{1}H NMR indicated starting material was fully converted. The reaction was stopped, and the solvent was removed using a rotvap under vacuum, the residue was diluted with EtOAc (25 mL) followed by water wash (3 X 10 mL). EtOAc layer was then dried using Na_2SO_4, then filtered and the solvent was removed under a vacuum to obtain a brownish liquid. This crude was further purified using column chromatography (Hexanes to 2% EtOAc/Hexanes) to obtain a brown solid as the desired product **3b** in 72.5 % yield, 537 mg, Rf = 0.38 (5% EtOAc/Hexanes).

Synthesis of compound **3c**

A mixture of benzaldehyde (1.0 g, 9.43 mmol, 1.0 equiv), $NH_2OH{\cdot}HCl$ (982.93 mg, 14.14 mmol, 1.5 equiv), and NaOAc (1.93 g, 23.27 mmol, 2.5 equiv) in ethanol (7.5 mL) and water (25 mL) was placed into a 100 mL round-bottomed flask with a reflux condenser. Then the reaction flask was heated to 95 ºC and the reaction progress was monitored by TLC (at 1 h point). After full conversion, the mixture was cooled to 0 ºC diluted with EtOAc (30 mL) and washed with water (5.0 mL X 2). The organic layer was then dried over anhydrous Na_2SO_4, filtered, and concentrated under a vacuum to obtain a crude product hydroxyl amine **2c**. This crude was directly taken to the next step. Compound **2c** (1.0 g, 8.25 mmol, 1.0 equiv) DMF (5.0 mL) was added NCS (1.1 g, 8.25 mmol, 1.0 equiv) dissolved in 5.0 mL DMF dropwise over a period of 1.0 h. The reaction was stirred for 12.0 h and at which time ^{1}H NMR showed disappearance of starting material. The solvent was removed under vacuum and diluted with EtOAc (25 mL) followed by water wash (2 X 10 mL). EtOAc layer was then dried over anh. Na_2SO_4 was filtered and the solvent was removed under a vacuum to obtain a yellowish liquid. Further purification was done by column

chromatography (Hexanes to 2% EtOAc) to obtain the product **3c** as a yellowish liquid in 71% yield, 915 mg.

Synthesis of compound **3d**

The hydroxyl amine **2d** was prepared first. A mixture of 4-chlorobenzaldehyde (1.0 g, 7.1 mmol, 1.0 equiv), $NH_2OH{\cdot}HCl$ (741.5 mg, 10.6 mmol, 1.5 equiv), and NaOAc (1.4 g, 17.7 mmol, 2.5 equiv) in ethanol (6.0 mL) and water (12.0 mL) was placed into a 100 mL round-bottomed flask with a reflux condenser. Then the reaction flask was heated to 95 ^oC and the reaction progress was monitored by ^1H NMR (at 2.0 h point), to see the disappearance of starting material. The reaction was stopped and cooled down to obtain white crystals which were filtered and washed with water to obtain the desired compound **2d**. It was taken to the next step without further purification. Compound **2d** (1.0 g, 6.42 mmol, 1.0 equiv) in anh. DMF (3.0 mL) was added NCS (858.3 mg, 6.42 mmol, 1.0 equiv) dissolved in 3.0 mL of anh. DMF dropwise over a period of 1.0 h at rt. The reaction was let stirred for 6.0 hours more and monitored by ^1H NMR to see the disappearance of starting material. The solvent was removed under vacuum and diluted with DCM (25 mL) followed by water wash (2 X 10 mL). DCM layer was then dried over anh. Na_2SO_4, was filtered and the solvent was removed under a vacuum to obtain the crude. This was further purified by column chromatography (Hexanes to 2% EtOAc/Hexanes) to obtain a white solid as desired product 84% yield, 1.02 g.

Synthesis of compound **3e**

The hydroxyl amine **2e** was prepared first. A mixture of 4-bromobenzaldehyde (1.0 g, 5.40 mmol, 1.0 equiv), $NH_2OH{\cdot}HCl$ (563.37 mg, 8.10 mmol, 1.5 equiv), and NaOAc (1.1 g, 13.5 mmol, 2.5

equiv) in ethanol (6.0 mL) and water (12.0 mL) was placed into a 100 mL round-bottomed flask with a reflux condenser. Then the reaction flask was heated to 95 ºC and the reaction progress was monitored by ^{1}H NMR (at 2.0 h point), to see the disappearance of starting material. The reaction was stopped and let it cool slowly to get the crystals. These crystals were filtered and washed with water to obtain the desired product. It was taken to the next step without further purification. Compound **2e** (1.0 g, 4.99 mmol, 1.0 equiv) in anh. DMF (5.0 mL) was added NCS (667.56 mg, 4.99 mmol, 1.0 equiv) dissolved in 5.0 mL of anh. DMF dropwise over a period of 1.0 h. The reaction was let to be stirred for 5.0 hours more and monitored by ^{1}H NMR to see the disappearance of starting material. The solvent was removed under vacuum and diluted with EtOAc (25 mL) followed by water wash (2 X 10 mL). EtOAc layer was then dried over anh. Na_2SO_4, was filtered and the solvent was removed under a vacuum to obtain a yellowish liquid. It was purified by recrystallization in Hexanes (adding 5 drops of EtOAc in 20 mL of Hexanes). (Yield 84%, 980 mg).

Synthesis of compound **3f**

The hydroxyl amine **2f** was prepared first. A mixture of 4-methoxy benzaldehyde (500 mg, 3.67 mmol, 1.0 equiv), $NH_2OH{\cdot}HCl$ (382.79 mg, 5.50 mmol, 1.5 equiv), and NaOAc (758.77 g, 9.25 mmol, 2.5 equiv) in ethanol (3.0 mL) and water (9.0 mL) was placed into a 100 mL round bottomed flask with a reflux condenser. Then the reaction flask was heated to 95 ºC and the reaction progress was monitored by ^{1}H NMR (at 2.0 h point), to see the disappearance of starting material. The reaction was stopped, EtOH was dried under a vacuum, DCM was added to the cloudy water solution, and the compound was extracted using a separatory funnel. The organic layer was dried over anhydrous Na_2SO_4, filtered and solvent was removed under vacuum to obtain brownish

viscous liquid which was taken directly to next step. Compound **2f** (1.0 g, 6.61 mmol, 1.0 equiv) in anh. DMF (5.0 mL) was added NCS (883.37 mg, 6.61 mmol. 1.0 equiv) dissolved in 5.0 mL of anh. DMF dropwise over a period of 1.0 h. The reaction was left stirred for 15 hours more and monitored by ^{1}H NMR to see the disappearance of starting material. The solvent was removed under vacuum and diluted with EtOAc (25 mL) followed by water wash (2 X 10 mL). EtOAc layer was then dried over anh. Na_2SO_4 was, filtered and the solvent was removed under a vacuum to obtain a brownish liquid. This brown liquid was further washed with water to obtain a crude compound as a yellowish liquid which was further purified by column chromatography (Hexanes to 2% EtOAc/Hexanes) to obtain a white fluffy solid as the desired product in 77% yield, 950 mg.

Synthesis of compound **3g**

The hydroxyl amine **2g** was prepared first. To a solution of compound 4-nitrobenzaldehyde (500 mg, 3.3 mmol, 1.0 equiv) in EtOH: H_2O (2:6 mL) was added hydroxylamine hydrochloride (344.8 mg, 4.96 mmol, 1.5 equiv) followed by sodium acetate (678.5 mg, 8.27 mmol, 2.5 equiv). The solution was refluxed for 2 hours to see the full conversion. The heating was stopped and slowly allowed to precipitate to obtain the desired product as a solid (480 mg, 88% by recrystallization).

Compound **2g** (300 mg, 1.80 mmol, 1.0 equiv) in anh. DMF (2.0 mL) was added NCS (241.13 mg, 1.8 mmol. 1.2 equiv) dissolved in 2.0 mL of anh. DMF dropwise over a period of 1.0 h. The reaction was left stirred for 15 hours more and monitored by ^{1}H NMR to see the disappearance of starting material. The solvent was removed under vacuum and diluted with EtOAc (25 mL) followed by water wash (2 X 10 mL). EtOAc layer was then dried over anh. Na_2SO_4 was, filtered and the solvent was removed under a vacuum to obtain a yellowish solid. This solid was further washed with water to obtain the desired compound as a white solid (290 mg, 80%).

Synthesis of compound **3h**

The hydroxyl amine **2h** was prepared first. To a solution of 3-Nitrobenzaldehyde (500 mg, 3.3 mmol, 1.0 equiv) in EtOH: H_2O (2:6 mL) was added hydroxylamine hydrochloride (344.8 mg, 4.96 mmol, 1.5 equiv) followed by sodium acetate (678.5 mg, 8.27 mmol, 2.5 equiv), refluxed for 2 h. The reaction mixture slowly precipitates to afford desired compound as a precipitate **2h**, 340 mg, 62%. Compound **2h** (300 mg, 1.80 mmol, 1.0 equiv) in DMF (2.0 mL), NCS (241.13 mg, 1.8 mmol. 1.2 equiv) dissolved in 2.0 mL DMF was added dropwise over a period of 1.0 h, stirred for 15 h. The crude was further purified by column chromatography 0-5% EtOAc/hexane to obtain white (312 mg, 86%).

Synthesis of compound **3i**

The hydroxyl amine **2i** was prepared first. 2,4-dichlorobenzaldehyde (1 g, 5.71 mmol, 1equiv), $NH_2OH.HCl$ (599.35 mg, 8.625 mmol, 1.5 equiv), along with NaOAc (1.17 g, 14.27 mmol, 2.5 equiv) was added with ethanol (6.0 mL) and water (12.0 mL), refluxed for 2 h at 95 °C. The reaction was stopped, and the mixture was cooled to slowly to allow for precipitation. The compound obtained was directly taken to the next step using similar procedure described above. Compound **2i** (1.0 g, 5.25 mmol, 1.0 equiv) in DMF (5.0 mL), NCS (706 mg, 5.25 mmol, 1.0 equiv) dissolved in DMF (5.0 mL) was added dropwise over 1.0 h. The reaction was stirred for 5h. The solvent was removed under vacuum and diluted with EtOAc (25 mL) followed by water wash (2 X 10 mL). The EtOAc layer was then dried over anh. Na_2SO_4 was, filtered and the solvent was removed on a rotavap under a vacuum to obtain the crude product, which was purified by column chromatography 0-5% EtOAc/Hexane to afford a white solid as the compound 3i in 89.9% yield, 891 mg, Rf= 0.45 10% EtOAc/Hexane.

Synthesis of compound **3j**

The hydroxyl amine **2j** was prepared first. To a mixture of 1-Naphthaldehyde (1 g (0.87 mL), 6.4 mmol, 1equiv), $NH_2OH.HCl$ (667 mg, 9.6 mmol, 1.5 equiv), and NaOAC (1.3 g, 16 mmol, 2.5 equiv) was added to a 100 mL round bottom flask. Ethanol (6.0 mL) and water (12.0 mL), refluxed for 2 h at 95 °C. The mixture was cooled slowly to allow for precipitation. The compound obtained was directly taken to the next step. Compound **2j** (1 g, 5.8 mmol, 1.0 equiv) in DMF (4.0 mL), NCS (1.8 mg, 13.2 mmol, 1.0 equiv) dissolved in 4.0 mL of DMF was added dropwise in 1.0 h. Then the reaction was left to be stirred for 5.0 hours more and monitored by ^1H NMR to see the disappearance of starting material. The solvent was removed under vacuum and diluted with EtOAc (25 mL) followed by water wash (2 X 10 mL). EtOAc layer was then dried over anh. Na_2SO_4, was filtered and the solvent was removed under a reduced pressure to get brown solid. Then column chromatography was performed at 0-10% (EtOAc/ Hexane) to obtain the product as a brown solid, in 82.6% yield (985 mg), Rf=0.35 (10% EtOAc/Hexane).

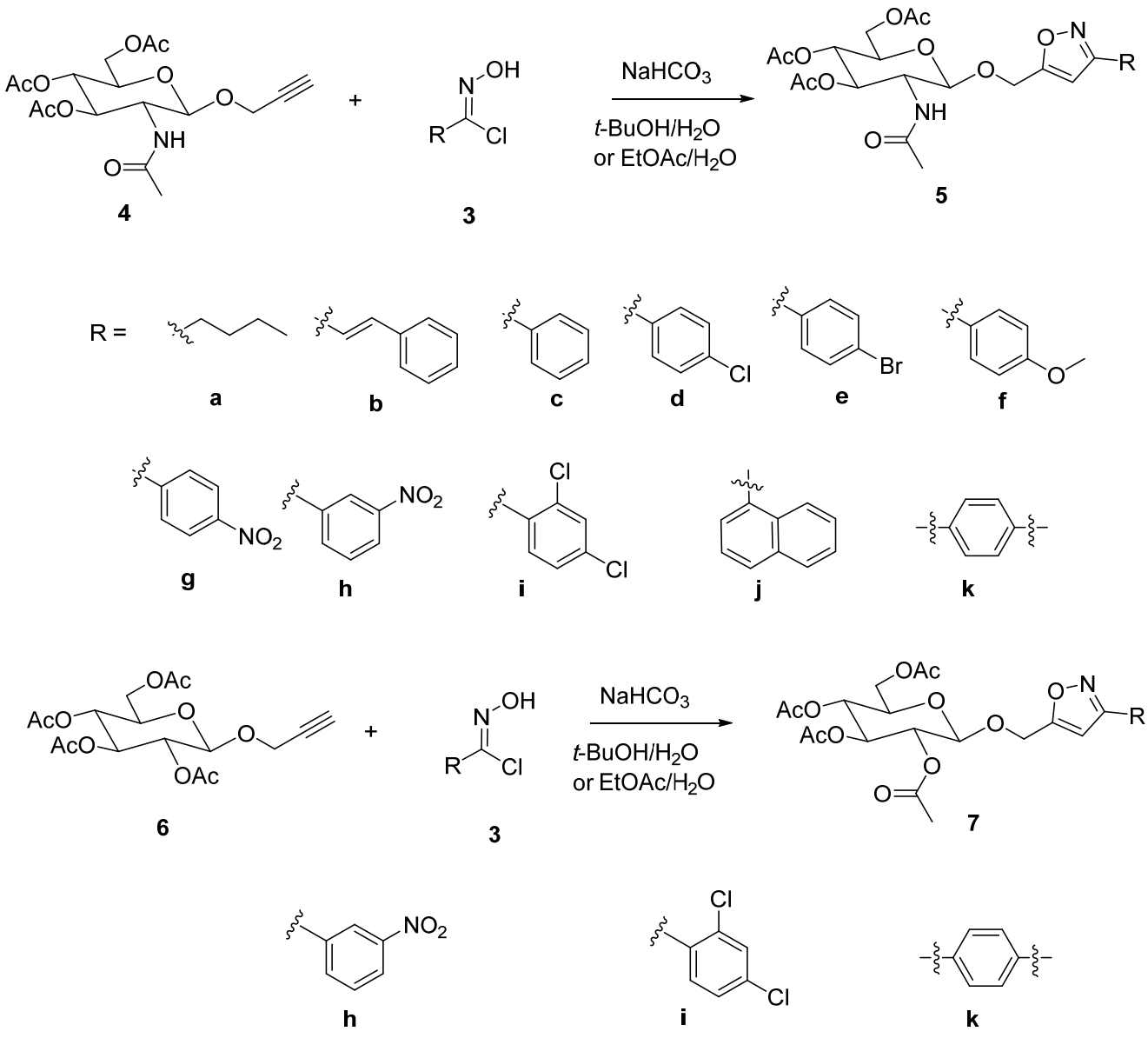
Synthesis of compound **3k**

The hydroxyl amine **2k** was prepared first. A mixture of terephthaldehyde (1.0 g, 7.46 mmol, 1.0 equiv), $NH_2OH{\cdot}HCl$ (1.6 mg, 22.37 mmol, 3.0 equiv), and NaOAc (3.1 g, 37.28 mmol, 5.0 equiv) in Ethanol (2.0 mL) and water (6.0 mL) was placed into a 100 mL round-bottomed flask with a reflux condenser at 95 ºC for 1 h. The reaction mixture was cooled to 0 ºC diluted with EtOAc (30 mL) and washed with water (5.0 mL X 2). The organic layer was then dried over anhydrous Na_2SO_4, filtered, and concentrated under a vacuum to obtain a crude product taken to the next step without further purification. Compound **2k** (300 mg, 1.80 mmol, 1.0 equiv)**,** DMF (4.0 mL), NCS (480 mg, 3.6 mmol. 2 equiv) dissolved in 3.0 mL DMF dropwise over a period of 1.0 h. The

reaction was left stirred for 12 h and monitored by ^{1}H NMR to see the disappearance of starting material. The solvent was removed under vacuum and diluted with EtOAc (25 mL) followed by water wash (2 X 10 mL). EtOAc layer was then dried over Na_2SO_4 and concentrated on a rotavap to obtain the crude product as an off-white slurry. This crude was further purified using column chromatography (Hexanes to 3% EtOAc/Hexanes) to obtain an off-white crystal as the desired compound. 51.2 % yield (728 mg), Rf = 0.41 (5% EtOAc/Hexanes).

II. Synthesis of isoxazole glycoconjugates

The follow section gives the detailed method for the synthesis of isoxazole for the first compound and only the amount used, and their characterization data were given the for others.



Scheme S2. Synthesis of isoxazoles **5a-5k**, **7h**, **7i**, **7k**.

Synthesis of compound 4: N-acetylglucosamine pentaacetate (1.0 g, 2.56 mmol, 1 equiv), 10 mL of DCE followed by TMSOTf (0.5 mL, 2.82 mmol, 1.1 equiv) at 0 °C and stirred for 1h at 50 °C. 1.0 g 4A° MS was added, after 30 min propargyl alcohol (0.3 mL, 5.13 mmol, 2 equiv) was added and stirred for 3h at 50 °C. The reaction was quenched with 0.6 mL of TEA. Aqueous workup was done using DCM. The crude was purified by column chromatography (0-2% MeOH/DCM) to obtain white solid as a desired product.

Synthesis of compound 5a: Valeraldehyde chloro oxime **3a** (105.5 mg, 0.77 mmol, 1.5 equiv) and EtOAc: H_2O (5.5 mL, v/v 1:0.1) was added along with, $NaHCO_3$ (65.4 mg, 0.77 mmol, 1.5 equiv) and sugar alkyne (**4,** 200.0 mg, 0.51 mmol, 1.0 equiv), stirred for 16 hours. The crude product solid was triturated in (5:1 Hexanes/EtOAc), to obtain the desired product as a white solid in 91% yield, 230 mg, m. p. 143.0 – 145.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.09 (s, 1H), 5.50 (d, J = 8.9 Hz, 1H), 5.25 (dd~t, J = 10.5, 9.6 Hz, 1H), 5.08 (t, J = 9.6 Hz, 1H), 4.86 (d, J = 13.8 Hz, 1H), 4.75 (d, J = 8.5 Hz, 1H, anomeric H), 4.71 (d, J = 13.8 Hz, 1H), 4.26 (dd, J = 12.4, 4.8 Hz, 1H), 4.15 (dd, J = 12.4, 2.4 Hz, 1H), 4.00 – 3.90 (m, 1H), 3.74 – 3.69 (m, 1H), 2.65 (t, J = 7.7 Hz, 2H), 2.09 (s, 3H), 2.023 (s, 3H), 2.021 (s, 3H), 1.91 (s, 3H), 1.67 – 1.59 (m, 2H), 1.44 – 1.34 (m, 2H), 0.93 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 170.6, 170.3, 169.3, 167.6, 164.2, 103.3, 100.2, 72.2, 72.1, 68.4, 62.0, 61.5, 54.5, 30.3, 25.6, 23.3, 22.2, 20.7, 20.63, 20.58, 13.7; HRMS (ESI+) m/z calcd for $[C_{22}H_{32}N_2O_{10}Na]^+$ $[M + Na]^+$: 507.1949, found 507.1945.

Synthesis of compound 5b: Cinnamaldehyde chloro oxime **3b** (70.7 mg, 0.38 mmol, 1.5 equiv) was added along with EtOAc: H_2O (v/v 5:0.5 mL), $NaHCO_3$ (87.2 mg, 1.03 mmol, 3.0 equiv) and sugar alkyne (**4,** 100.0 mg, 0.25 mmol, 1.0 equiv), stirred for 16 h. The crude product was purified

by column chromatography (DCM to 1.5% MeOH/DCM) to obtain the desired product as a white solid in 70% yield, 96 mg. R_f: 0.26 (3% MeOH/DCM). m. p. 178.0 – 179.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 2H), 7.42 – 7.31 (m, 3H), 7.18 (d, J = 16.5 Hz, 1H), 7.10 (d, J = 16.5 Hz, 1H), 6.51 (s, 1H), 5.52 (d, J = 8.9 Hz, 1H), 5.29-5.23 (dd~t, J = 10.4, 9.4 Hz, 1H), 5.11 (t, J = 9.7 Hz, 1H), 4.91 (d, J = 13.8 Hz, 1H), 4.79 (d, J = 8.4 Hz, 1H anomeric H), 4.78 (d, J = 13.8 Hz, 1H), 4.31 – 4.25 (dd, J = 12.4, 4.8 Hz, 1H), 4.20 – 4.15 (dd, J = 12.4, 2.5 Hz, 1H), 4.02 – 3.93 (m, 1H), 3.77 – 3.71 (m, 1H), 2.10 (s, 3H), 2.033 (s, 3H), 2.030 (s, 3H), 1.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 170.7, 170.3, 169.3, 167.9, 161.8, 136.4, 135.7, 129.1, 128.9, 127.0, 115.7, 100.8, 100.3, 72.2 (2C), 68.4, 62.0, 61.5, 54.5, 23.3, 20.7, 20.64, 20.59; HRMS (ESI+) m/z calcd for $[C_{26}H_{30}N_2O_{10}Na]^+$ $[M + Na]^+$: 553.1793, found 553.1793.

Synthesis of compound 5c: Benzaldehyde chloro oxime **3c** (60.55 mg, 0.38 mmol, 1.5 equiv), EtOAc: H_2O (4.0:0.5 mL), $NaHCO_3$ (32.6 mg, 0.38 mmol, 1.5 equiv) and sugar alkyne (**4,** 100.0 mg, 0.26 mmol, 1.0 equiv) was added and stirred for 24 h. Compound was purified by column chromatography (DCM to 1.0% MeOH/DCM) to obtain a white solid as desired product, in 82% yield, 108 mg. R_f: 0.17 (3% MeOH/DCM). m. p. 166.0 – 167.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82-7.76 (m, 2H), 7.48 – 7.42 (m, 3H), 6.58 (s, 1H), 5.57 (d, J = 8.8, 1H, NH), 5.30-5.23 (dd, J = 10.6, 9.4 Hz, 1H H-3), 5.10 (dd~t, J = 9.6, 1H, H-4), 4.94 (d, J = 13.8 Hz, 1H), 4.82 (d, J = 8.4 Hz, H-1) Hz, 4.91 (d, J = 13.8 Hz, 1H), 4.31-4.24 (dd, J = 12.4, 4.8 Hz, 1H), 4.20-4.14 (dd, J = 12.4, 2.5 Hz, 1H), 4.03 – 3.93 (m, 1H), 3.78 – 3.71 (m, 1H), 2.00 (s, 3H), 2.03 (br, s, 6H), 1.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 170.6, 170.3, 169.3, 168.6, 162.5, 130.2, 129.0, 128.7, 126.8, 101.8, 100.2, 72.2, 68.4, 62.0, 61.5, 54.5, 23.3, 20.7, 20.63, 20.59; HRMS (ESI+) m/z calcd for $[C_{24}H_{28}N_2O_{10}Na]^+$ $[M + Na]^+$: 527.1636, found 527.1637.

Synthesis of compound 5d: 4-chloro benzaldehyde chloro oxime **3d** (73.9 mg, 0.38 mmol, 1.5 equiv), EtOAc: H_2O (v/v 5.0:0.5 mL), $NaHCO_3$ (87.2 mg, 1.03 mmol, 4.0 equiv) and sugar alkyne (**4,** 100.0 mg, 0.25 mmol, 1.0 equiv) were added and mixture stirred for 15 h. The reaction was stopped, and 6.0 mL of hexanes was added to the reaction mixture and triturated to obtain a white solid as desired production 75% yield, 105 mg. m. p. 185.0 – 187.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.70 (m, 2H), 7.46 – 7.41 (m, 2H), 6.55 (s, 1H), 5.59 (d, J = 8.8 Hz, 1H), 5.30-5.23 (dd, J = 10.6, 9.4 Hz, 1H), 5.09 (dd~t, J = 9.7 Hz, 1H), 4.94 (d, J = 13.8 Hz, 1H), 4.82 (d, J = 8.4 Hz, 1H, anomeric), 4.80 (d, J = 13.8 Hz, 1H), 4.31-4.23 (dd, J = 12.4, 4.8 Hz, 1H), 4.20-4.12 (dd, J = 12.4, 2.5 Hz, 1H), 4.00 – 3.90 (m, 1H), 3.78 – 3.70 (m, 1H), 2.08 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 1.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 170.6, 170.3, 169.3, 169.0, 161.5, 136.2, 129.3, 128.1, 127.2, 101.6, 100.3, 72.2, 72.1, 68.4, 62.0, 61.5, 54.5, 23.3, 20.7, 20.62, 20.57; HRMS (ESI+) m/z calcd for $[C_{24}H_{27}ClN_2O_{10}Na]^+$ $[M + Na]^+$: 561.1246, found 561.1248.

Synthesis of compound 5e: 4-Bromo benzaldehyde chloro oxime **3e** (91.2 mg, 0.38 mmol, 1.5 equiv), *t*-BuOH: H_2O (5.0 mL) were added a 50 mL round bottom flash. To this solution, $NaHCO_3$ (32.6 mg, 0.38 mmol, 1.5 equiv) and sugar alkyne (**4,** 100.0 mg, 0.25 mmol, 1.0 equiv) were added and the mixture was stirred for 23 h. The solvent was dried under reduced pressure. Further purification was done by recrystallization in EtOH: H_2O (v/v, 5:1) to obtain a white solid as the desired product in 73% yield, 110 mg, m. p. 194.0 – 196.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69-7.64 (m, 2H), 7.62 -7.57 (m, 2H), 6.56 (s, 1H), 5.56 (d, J = 8.7, 1H), 5.28 (dd~t, J = 9.9, 1H), 5.10 (dd~t, J = 9.6 Hz, 1H), 4.95 (d, J = 13.8, 1H), 4.82 (d, J = 8.3 Hz, 1H, anomeric), 4.80 (d, J = 13.8 Hz, 1H), 4.32-4.23 (dd, J = 12.4, 4.8 Hz, 1H), 4.21-4.13 (dd, J = 12.4, 2.2 Hz, 1H), 4.00 –

3.91 (m, 1H), 3.78 – 3.70 (m, 1H), 2.08 (s, 3H), 2.031 (s, 3H), 2.028 (s, 3H), 1.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 170.6, 170.3, 169.3, 169.0, 161.6, 132.2, 128.3, 127.7, 124.5, 101.5, 100.3, 72.2, 72.1, 68.4, 62.0, 61.5, 54.5, 23.3, 20.7, 20.63, 20.59; HRMS (ESI+) *m*/*z* calcd for $C_{24}H_{27}BrN_2O_{10}Na$ $[M + Na]^+$: 605.0741, found 605.0737.

Synthesis of compound 5f: 4-Methoxy benzaldehyde chloro oxime **3f** (72.2 mg, 0.38 mmol, 1.5 equiv), EtOAc/H_2O (v/v 10:1, 5.0 mL). $NaHCO_3$ (32.6 mg, 0.38 mmol, 1.5 equiv) and sugar alkyne (**4,** 100.0 mg, 0.25 mmol, 1.0 equiv) were added and the mixture was stirred for 12 h. The solvent was dried under reduced pressure and the crude was purified using column chromatography (DCM to 3% MeOH/DCM) to obtain a yellowish solid. This was further purified by trituration using 50% EtOAc/Hexanes to obtain white solid as desired product. 70% yield, 97 mg. R_f: 0.32 (4% MeOH/DCM). m. p. 179.0 – 181.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.70 (m, 2H), 7.00 – 6.95 (m, 2H), 6.52 (s, 1H), 5.54 (d, *J* = 8.9, 1H), 5.30-5.22 (dd, *J* = 10.6, 9.4 Hz, 1H), 5.09 (dd~t, *J* = 9.7 Hz, 1H), 4.93 (d, *J* = 13.8 Hz, 1H), 4.81 (d, *J* = 8.4 Hz, 1H, anomeric), 4.79 (d, *J* = 13.8 Hz, 1H), 4.31-4.24 (dd, *J* = 12.4, 4.8 Hz, 1H), 4.20-4.14 (dd, *J* = 12.4, 2.3 Hz, 1H), 4.02 – 3.92 (m, 1H), 3.86 (s, 3H), 3.77 – 3.70 (m, 1H), 2.09 (s, 3H), 2.03 (br, s, 6H), 1.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 170.7, 170.3, 169.3, 168.3, 162.1, 161.2, 128.2, 121.2, 114.4, 101.6, 100.2, 72.20, 72.16, 68.4, 62.0, 61.5, 55.4, 54.5, 23.3, 20.7, 20.63, 20.59; HRMS (ESI+) *m*/*z* calcd for $C_{25}H_{30}N_2O_{11}Na$ $[M + Na]^+$: 557.1742, found 557.1741.

Synthesis of compound 5g: 4-Nitro benzaldehyde chlorooxime **3g** (78.1 mg, 0.39 mmol, 1.5 equiv), EtOAc/H_2O (v/v 10:1, 5.0 mL), then $NaHCO_3$ (87.19 mg, 1.03 mmol, 4.0 equiv) and sugar alkyne (**4,** 100.0 mg, 0.26 mmol, 1.0 equiv) were added and the mixture stirred for 8 h. The solvent

was dried under reduced pressure, and further purified by column chromatography (DCM to 0.5% MeOH/DCM) to obtain a white solid as desired product in 88% yield (126 mg), R_f = 0.24 (3% MeOH/DCM). m. p. 199.0 – 201.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 – 8.31 (m, 2H), 8.01 – 7.97 (m, 2H), 6.67 (s, 1H), 5.49 (d, J = 8.8 Hz, 1H), 5.32-5.24 (dd, J = 10.6, 9.4 Hz, 1H), 5.11 (dd~t, J = 9.7 Hz, 1H), 4.98 (d, J = 13.8 Hz, 1H), 4.84 (d, J = 8.4 Hz, 1H, anomeric), 4.83 (d, J = 13.8 Hz, 1H), 4.31-4.24 (dd, J = 12.4, 4.8 Hz, 1H), 4.21-4.16 (dd, J = 12.4, 2.5 Hz, 1H), 4.00 – 3.91 (m, 1H), 3.79 – 3.72 (m, 1H), 2.09 (s, 3H), 2.044 (s, 3H), 2.038 (s, 3H), 1.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 170.6, 170.3, 169.8, 169.3, 160.7, 148.8, 134.8, 127.7, 124.3, 100.7, 100.4, 72.3, 72.0, 68.3, 61.9, 61.5, 54.6, 23.3, 20.7, 20.63, 20.59; HRMS (ESI+) m/z calcd for $C_{24}H_{27}N_3O_{12}Na$ $[M + Na]^+$: 572.1487, found 572.1489.

Synthesis of compound 5h: 3-Nitro benzaldehyde chloro oxime **3h** (78.1 mg, 0.39 mmol, 1.5 equiv) dissolved in EtOAc/H_2O (v/v 10:1, 5.0 mL). $NaHCO_3$ (87.19 mg, 1.03 mmol, 4.0 equiv) and sugar alkyne (**4,** 100.0 mg, 0.26 mmol, 1.0 equiv) were added and the mixture was stirred for 8 h. The crude was rinsed with H_2O (1.0 mL) and hexanes (2.0 mL) following by filtration to obtain a white solid as the desired product, yield 79% (112 mg) R_f: 0.22 (3% MeOH/DCM). m. p. 159.0 – 161.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.31 (m, 1H), 8.16 (d, J = 7.7, 1H), 7.67 (t, J = 8.0 Hz, 1H), 6.69 (s, 1H), 5.60 (d, J = 8.9 Hz, 1H), 5.29 (t, J = 9.9 Hz, 1H), 5.10 (dd~t, J = 9.6 Hz, 1H), 4.98 (d, J = 13.8 Hz, 1H), 4.90- 4.80 (m, 2H), 4.32-4.24 (dd, J = 12.4, 4.5 Hz, 1H), 4.21-4.16 (dd, J = 12.4, 1.8 Hz, 1H), 4.02 – 3.90 (m, 1H), 3.81 – 3.70 (m, 1H), 2.09 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 1.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 170.6, 170.4, 169.8, 169.3, 160.7, 148.7, 132.5, 130.6, 130.1, 124.7, 121.8, 101.6, 100.3, 72.3, 72.0, 68.4, 61.9, 61.5,

54.6, 23.3, 20.7, 20.64, 20.58; HRMS (ESI+) *m/z* calcd for $C_{24}H_{27}N_3O_{12}Na$ $[M + Na]^+$: 572.1487, found 572.1487.

Synthesis of compound 5i: 2,4-Dichlorophenylchlorooxime **3i** (84 mg, 0.39 mmol, 1.5 equiv) was added along with EtOAc/H_2O (v/v 10:1, 5.0 mL). $NaHCO_3$ (84 mg, 1 mmol, 4.0 equiv) and sugar alkyne (**4**, 100.0 mg, 0.26 mmol, 1.0 equiv) was added and stirred for 18 h to see the complete consumption of starting material. The solvent was dried, and the crude was recrystallized in isopropanol. Yield: 79% (112 mg), R_f = 0.45 (5% MeOH/DCM). m. p. 198.0 – 199.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.4 Hz, 1H), 7.51 (d, *J* = 2.0 Hz, 1H), 7.35 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.72 (s, 1H), 5.58 (d, *J* = 8.3 Hz, 1H), 5.28 (t, *J* = 9.8 Hz, 1H), 5.09 (t, *J* = 9.5 Hz, 1H), 4.96 (d, *J* = 13.5 Hz, 1H), 4.88-4.77 (m, 2H), 4.31-4.23 (dd, *J* = 12.4, 4.6 Hz, 1H), 4.19-4.12 (m, 1H), 4.01-3.90 (m, 1H), 3.78-3.69 (m, 1H), 2.08 (s, 3H), 2.02 (br, s, 6H), 1.93(s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 170.6, 170.3, 169.3, 168.2, 160.2, 136.5, 133.5, 131.7, 130.3, 127.6, 126.5, 104.8, 100.1, 72.2, 72.1, 68.4, 61.9, 61.3, 54.5, 23.3, 20.7, 20.6, 20.5; HRMS (ESI+) *m/z* calcd for $C_{24}H_{26}Cl_2N_2O_{10}Na$ $[M + Na]^+$: 595.0857, found 595.0850.

Synthesis of compound 5j: 2-Napthylchloro-oxime (80 mg, 0.39 mmol, 1.5 equiv) was added along with EtOAc/H_2O (v/v 10:1, 5.0 mL), $NaHCO_3$ (84 mg, 1 mmol, 4.0 equiv) and sugar alkyne (**4**, 100.0 mg, 0.26 mmol, 1.0 equiv) was added and stirred for 15 h. The crude was recrystallized in ethanol to obtain as a desired product as a white solid in 84% yield, 121 mg; R_f = 0.47 (5% MeOH/DCM); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39-8.34 (m, 1H), 8.00-7.92 (m, 2H), 7.73-7.69 (m, 1H), 7.59-7.54 (m, 3H), 6.62 (s, 1H), 5.59 (d, *J* = 8.8 Hz, 1H), 5.33 (dd, *J* = 10.5 Hz, 9.4Hz 1H), 5.13 (dd~t, *J* = 9.7 Hz, 1H), 5.04 (d, *J* = 13.8 Hz, 1H), 4.89 (d, *J* = 8.9 Hz, 1H anomeric),

4.88 (d, J = 13.8 Hz, 1H), 4.29 (dd, J = 12.4 Hz, 4.8 Hz, 1H), 4.18 (dd, J = 12.4 Hz, 2.5 Hz 1H), 4.03-3.92 (m, 1H), 3.81-3.71 (m, 1H), 2.09 (s, 3H), 2.05 (br, s, 6H), 1.95 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 170.6, 170.3, 169.3, 167.9, 162.6, 133.8, 130.9, 130.4, 128.5, 127.8, 127.1, 126.4, 126.3, 125.4, 125.1, 105.0, 100.2, 72.2, 72.1, 68.4, 61.9, 61.5, 54.6, 23.3, 20.7, 20.65, 20.6; HRMS (ESI+) m/z calcd for $C_{28}H_{30}N_2O_{10}Na$ $[M + Na]^+$: 557.1793, found 577.1790.

Synthesis of compound 5k: Terephthalaldehyde chlorooxime **3k** (50.0 mg, 0.21 mmol, 1.0 equiv) was added along with EtOAc/H_2O (v/v 10:1, 5.0 mL), $NaHCO_3$ (90.0 mg, 1.07 mmol, 5.0 equiv) and sugar alkyne (**4,** 165 mg, 0.43 mmol, 2.0 equiv) were added and stirred for 8 h. The crude was further purified by trituration (EtOAc: Hexanes: MeOH, 10:3:1) to obtain a white solid as the desired product in 72 % yield, 143 mg, R_f = 0.23 (5% MeOH/DCM); m.p. ^{1}H NMR (400 MHz, d_6-DMSO) δ 8.01-7.98 (m, 6H), 7.08 (s, 2H), 5.13 (t, J = 9.8 Hz, 2H), 4.96-4.78 (m, 8H), 4.24-4.17 (dd, J = 12.4 Hz, 4.8 Hz, 2H), 4.10-4.13 (dd, J = 12.4 Hz, 2.3 Hz, 2H), 3.93-3.86 (m, 2H), 3.85-3.75 (m, 2H), 2.02 (s, 6H), 1.98 (s, 6H), 1.92 (s, 6H), 1.77 (s, 6H). ^{13}C NMR (100 MHz, d6-DMSO) δ 170.0, 169.6, 169.4, 169.3, 169.2, 161.2, 130.0, 127.3, 102.0, 99.7, 72.8, 72.4, 68.5, 61.7, 60.8, 53.0, 22.6, 20.43, 20.35, 20.26; HRMS (ESI+) m/z calcd for $C_{42}H_{50}N_4O_{20}Na$ $[M + Na]^+$: 953.2911, found 953.2899.

Synthesis of compound 6: D-glucose pentaacetate (1 g, 2.56 mmol, 1 equiv) was dissolved in DCM (7.0 mL) and propargyl alcohol (0.22 mL, 3.84 mmol, 1.5 equiv) was added along with $BF_3.Et_2O$ (0.57 mL, 4.6 mmol, 1.8 equiv) at 0 °C, stirred for 16h. The reaction was quenched with 5% $NaHCO_3$. The crude was further purified using column chromatography to obtain white solid as a desired product in 60% yield, 550 mg.

Synthesis of compound 7h: 3-Nitro benzaldehyde chloro oxime **3h** (77.9 mg, 0.39 mmol, 1.5 equiv) was added along with EtOAc/H_2O (v/v 10:1, 5.5 mL, $NaHCO_3$ (87.0 mg, 1.03 mmol, 4.0 equiv) and sugar alkyne **6** (100.0 mg, 0.26 mmol, 1.0 equiv), stirred for 8 h. The crude product was triturated with H_2O (1.0 mL) and hexanes (2.0 mL) to obtain a white solid as desired product in 86% yield, 118 mg; R_f: 0.45 (50% EtOAc/Hexanes). m. p. 164.0 – 165.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.34-8.28 (m, 1H), 8.17 (d, J = 8.0 Hz, 1H), 7.67 (t, J = 8.0 Hz, 1H), 6.67 (s, 1H), 5.22 (dd~t, J = 9.6 Hz, 1H), 5.16 – 5.04 (m, 2H), 4.96 (d, J = 14.0 Hz, 1H), 4.84 (d, J = 14.0 Hz, 1H), 4.69 (d, J = 7.8 Hz, 1H, anomeric), 4.33-4.24 (dd, J = 12.4, 4.8 Hz, 1H), 4.22-4.15 (dd, J = 12.4, 2.4 Hz, 1H), 3.80 – 3.73 (m, 1H), 2.09 (s, 3H), 2.05 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 170.1, 169.5, 169.33, 169.28, 160.6, 148.7, 132.5, 130.5, 130.1, 124.7, 121.8, 101.4, 100.1, 72.6, 72.2, 71.0, 68.2, 61.7, 61.6, 20.7, 20.6, 20.5; HRMS (ESI+) m/z calcd for $[C_{24}H_{26}N_2O_{13}Na]^+$ $[M + Na]^+$: 573.1327, found 573.1327.

Synthesis of compound 7i: 2,4-Dichlorophenylchlorooxime **3i** (87.54 mg, 0.39 mmol, 1.5 equiv) was added along with EtOAc/H_2O (v/v 10:1, 5.0 mL), $NaHCO_3$ (84 mg, 1 mmol, 4.0 equiv) and alkyne **6** (100.0 mg, 0.26 mmol, 1.0 equiv), stirred for 15 h. Then the crude product was purified using column chromatography 0-5% MeOH/DCM to get clear oily appearances in 68.0% yield, 101 mg. R_f=0.47 (5% MeOH/DCM); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.4 Hz, 1H), 7.51 (d, J = 2.1 Hz, 1H), 7.36 (dd, J = 8.4, 2.1 Hz), 6.72 (s, 1H), 5.22 (t, J = 9.4 Hz, 1H), 5.15 – 5.03 (m, 2H), 4.95 (d, J = 14.0 Hz, 1H), 4.83 (d, J = 14.0 Hz, 1H), 4.67 (d, J = 7.8 Hz, 1H), 4.31-4.24 (dd, J = 12.5, 4.8 Hz, 1H), 4.20-4.13 (dd, J = 12.5, 2.5 Hz, 1H), 3.77 – 3.71 (m, 1H), 2.09 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 170.2, 169.4, 169.3,

168.0, 160.2, 136.5, 133.6, 131.7, 130.3, 127.7, 126.6, 104.7, 99.7, 72.6, 72.2, 71.0, 68.2, 61.8, 61.6, 20.7, 20.6, 20.56 (2C).

Synthesis of compound 7k: Compound **3k** (30 mg, 0.13 mmol, 0.5 equiv) was added along with EtOAc/H_2O (v/v 10:1, 5.0 mL), $NaHCO_3$ (84 mg, 1 mmol, 4.0 equiv) and sugar alkyne **6** (100 mg, 0.26 mmol, 1.0 equiv), stirred for 15 h. The crude was recrystallized in toluene and hexane to afford the desired product as a white solid in 78.5% yield, 95 mg. R_f = 0.67 (85% EtOAc/Hexane), m.pt. 141.0-143.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 4H), 6.61 (s, 2H), 5.22 (t, J = 9.4 Hz, 2H), 5.12 (dd~t, J = 9.7 Hz, 2H), 5.09-5.04 (dd, J = 8.0, 9.6 Hz, 2H), 4.95 (d, J = 13.9 Hz, 2H), 4.83 (d, J = 13.9 Hz, 2H), 4.69 (d, J = 7.9 Hz, 2H), 4.31-4.24 (dd, J = 12.4, 4.8 Hz, 2H), 4.20-4.15 (dd, J = 12.4, 2.4 Hz, 2H), 3.78-3.72 (m, 2H), 2.09 (s, 6H), 2.04 (s, 6H), 2.03 (s, 6H), 2.01 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 170.1, 169.4, 169.3, 168.7, 161.7, 130.4, 127.4, 101.5, 100.0, 72.6, 72.2, 71.0, 68.2, 61.8, 61.7, 20.7, 20.6, 20.56 (2C); HRMS (ESI+) *m*/*z* calcd for $[C_{42}H_{48}N_2O_{22}Na]^+$ $[M + Na]^+$: 955.2591, found 955.2590.

III. Additional gelation analysis

1. Further gelation test for compound **5d**.

Compound **5d** formed a hydrogel at 1.1 mg/mL, or 0.11 wt%, this compound was tested for spontaneous gelation in DMSO/water mixtures. 2.0 mg of compound **5d** was dissolved in DMSO (0.1 mL) in a one-dram vial, then 0.1 mL water was added to the vial, spontaneous gelation occurred at rt to give a translucent gel. To this sample, 0.1 mL water was added until a stable gel could no longer form. The gelator formed gels at 1:2 and 1:3 DMSO/water ratio and gelation concentration of 5.0 mg/mL for 1:3 DMSO-water mixture.

Metallogel tests for compound **5d**

The minimum gelation concentration of **5d** for the gelation in the presence of 1 equivalent metal ions to gelator was analyzed. For this experiment, 2.0 mg of compound **5d** was dissolved in aqueous metal ion stock solution (0.1 mL) and DI H_2O in a one-dram vial, followed by the incremental addition of water (0.1 mL) until a stable gel could no longer form. Aqueous metal ion stock solutions were prepared by dissolving $NiCl_2$, $Zn(OAc)_2 \cdot 2H_2O$, $Cu(OAc)_2 \cdot H_2O$ (20.0 equiv, 1.0 equiv per 0.1 mL) in DI water (2.0 mL) using 2 mL volumetric flasks. The gels were opaque and stable at 0.9 mL water, gelation concentrations at 2.0 mg/mL; additional water was added to the same vials and the gelator formed gels at up to total 1.8 mL water, giving final MGC 1.1 mg/mL, for Ni and Cu, some liquid was observed on top of the gels, but for Zn, the gel was more stable and very little residue water was observed on the gel, as shown in Figure S1 (a-c).

In addition to these, we also tested the gelation properties of compound 5d in the presence of different metal salts included $ZnCl_2$, $CuCl_2$, $HgCl_2$ and $Pb(NO_3)_2$. The compound formed stable gels as well, these are shown in Figure S1(d-g).

2. Gelation test for two component gelators **5g** and **5f**

A mixture of gelators (1:1 molar ratios) were prepared using compounds **5f** and **5g** (2.0 mg + 1.9 mg). The mixtures were tested using incremental additions of solvent until a stable gel could no longer form. The mixture of **5f** and **5h** (2.0 mg + 1.9 mg) was also preprepared and tested in water, it was able to form stable hydrogel at 13.0 mg/mL.

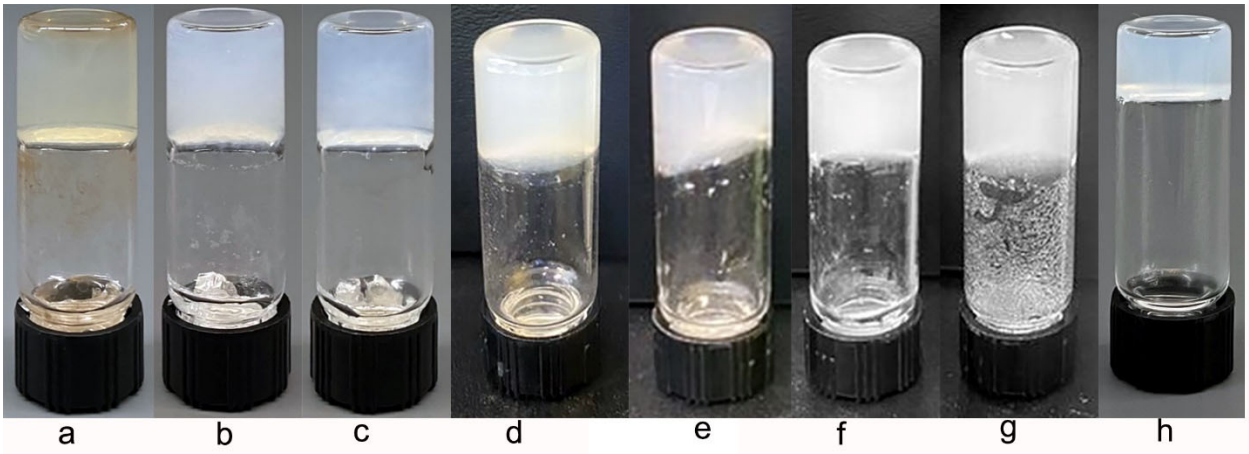


Figure S1. The photographs of the metallogels formed by compound **5d** in water at concentration 1.1 mg/mL with 1.0 equivalent of metal ions: (a) $Cu(OAc)_2$, (b) with $Zn(OAc)_2$, (c) with $NiCl_2$. (d) with $ZnCl_2$, (e) with $CuCl_2$, (f) with $HgCl_2$, (g) with $Pb(NO_3)_2$. (h) A gel formed by **5f** and **5g** at 4.3 mg/mL in EtOH:H_2O (v/v 1:2).

3. ^{1}H NMR spectroscopy for compound **5h** at different concentrations

The gelation mechanism was probed using ^{1}H NMR spectroscopy at variable concentrations, the spectra are shown in Figure S2. The ^{1}H NMR spectra of the compound **5h** at different concentrations showed that the amide NH signal shifting when concentration is increased, which is attributed to the intermolecular hydrogen bonding.

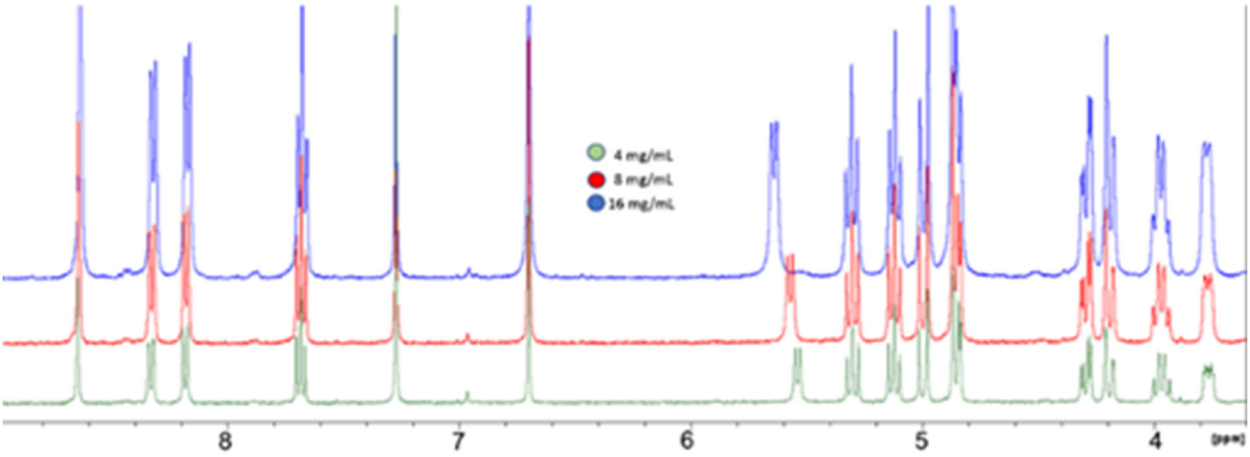


Figure S2. ^{1}H NMR spectra of compound **5h**, 400 MHz, $CDCl_3$.

IV. Rheological studies for hydrogels formed by gelator 5d and 5h

The rheological properties of the hydrogels formed by gelator **5d** and **5h** are shown in Figures S3 and Figure 4, respectively. The amplitude and frequency sweep data are included for all gels. The storage modulus and loss modulus as well as the ratio of G'/G" are included in the table following the graphs. As shown in Figure S3, for all three hydrogels of **5d** at different concentrations, the storage modulus G′ is greater than the loss modulus G″ for all samples. The storage moduli G′ exhibited concentration dependent, higher concentrations correlate to larger values, which also indicate the gels are more stable at the higher concentrations. The loss moduli showed concentrations dependence, at 1.1 mg/mL it has much lower values comparing to the 2.2 and 4.4 mg/mL gels, which gave similar results.

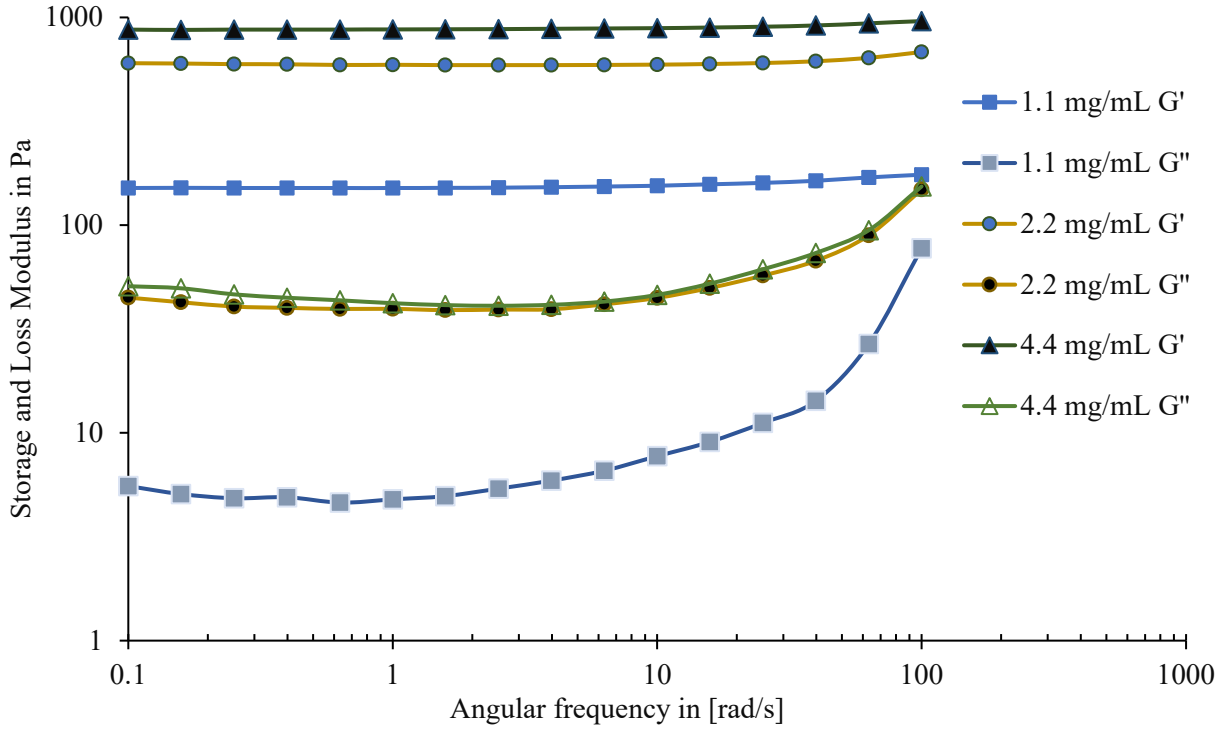
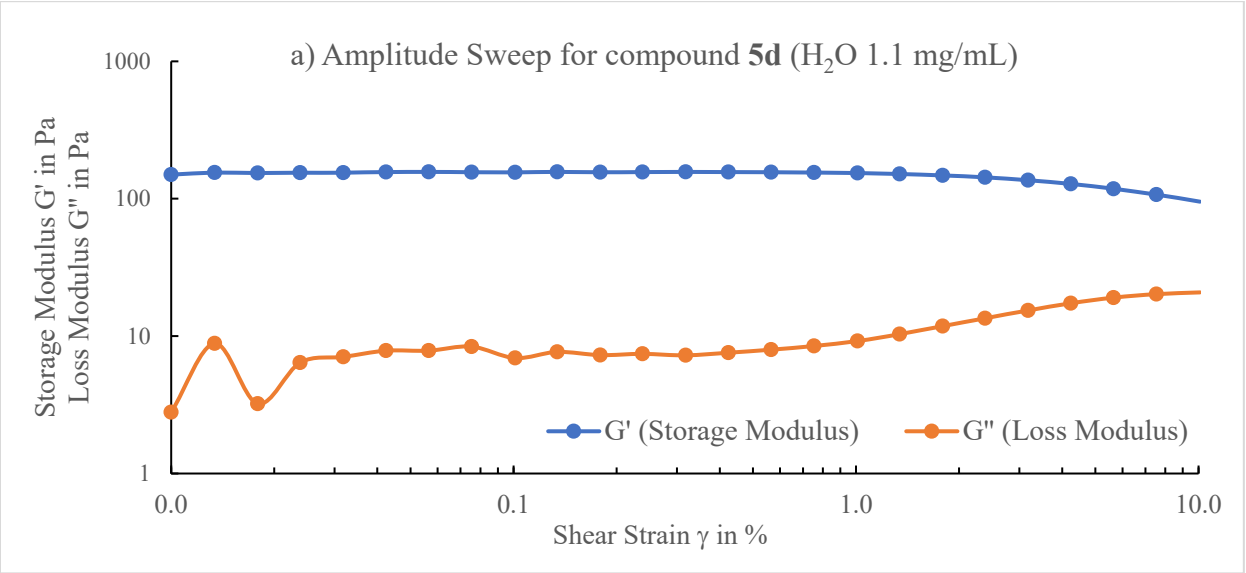


Figure S3. Rheology properties of several hydrogels formed by **5d** at gelation concentrations of 1.1 mg/mL, 2.2 mg/mL, and 4.4 mg/mL.

1. Rheology data for compound **5d** in water at 1.1 mg/mL



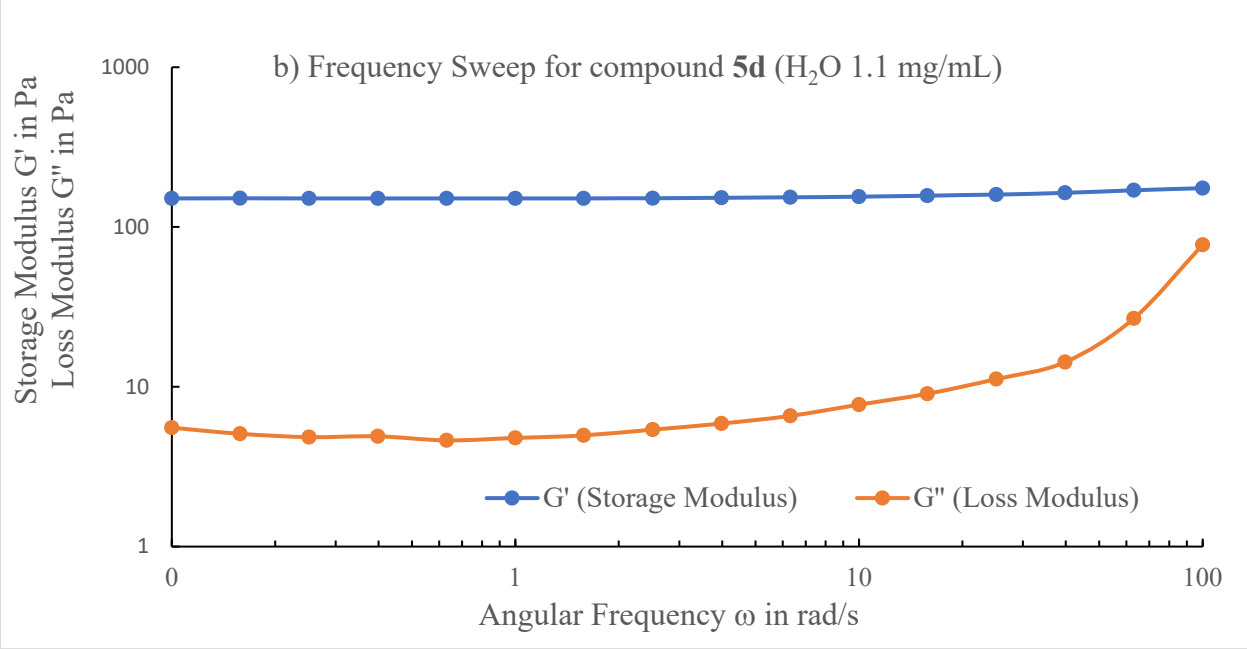
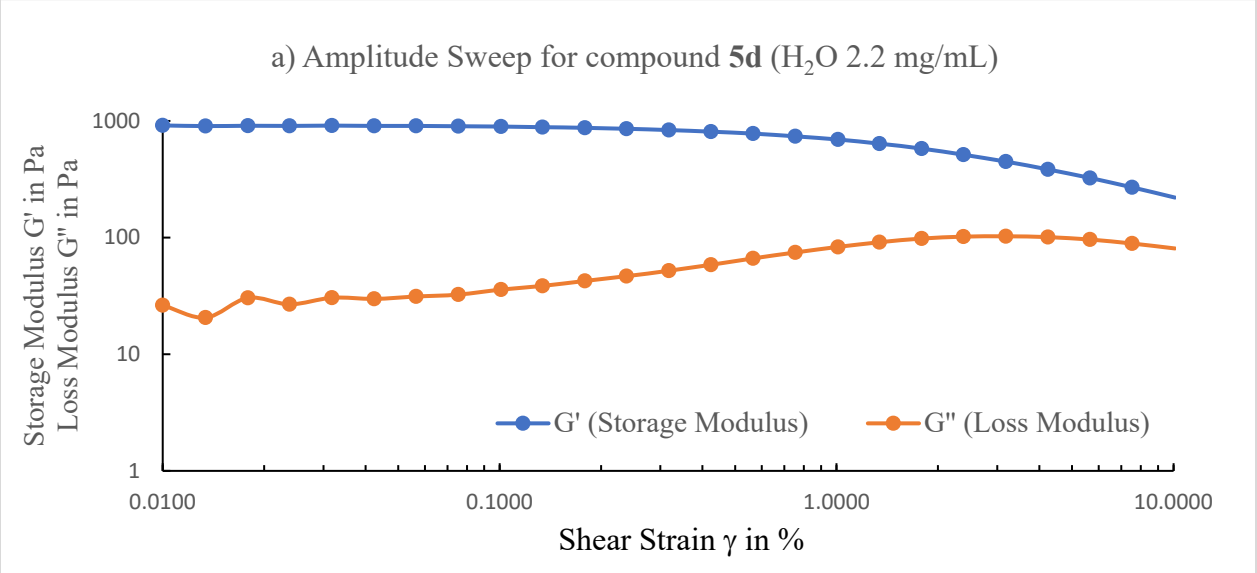


Figure S4. Amplitude sweep (a) and frequency sweep (b) for the hydrogel formed by compound **5d** at 1.1 mg/mL.

2. Rheology data for compound **5d** in water at 2.2 mg/mL



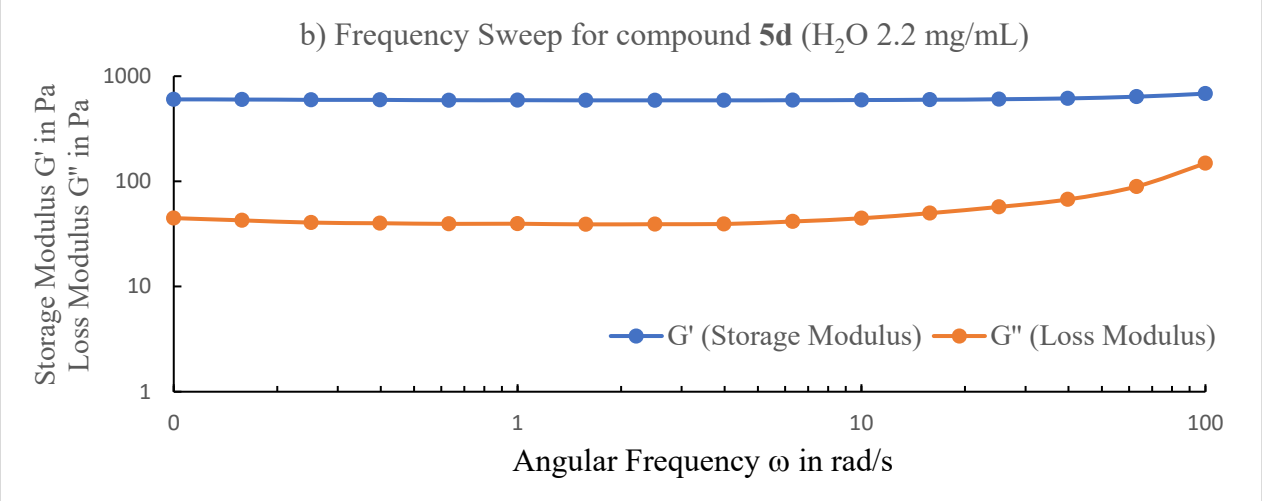
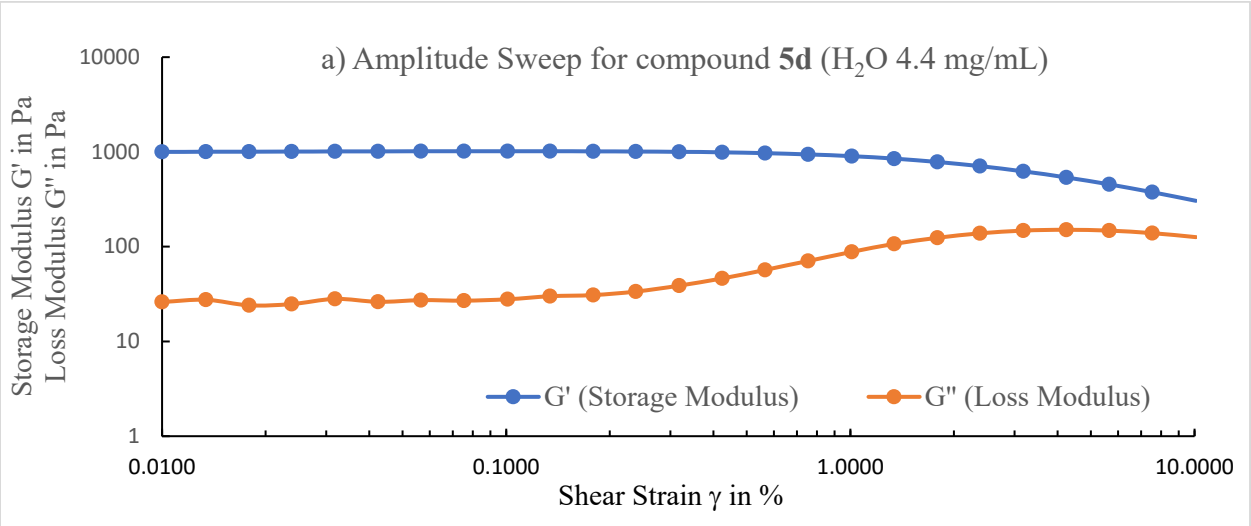


Figure S5. Amplitude sweep (a) and frequency sweep (b) for the hydrogel formed by compound **5d** at 2.2 mg/mL.

3. Rheology data for compound **5d** in water at 4.4 mg/mL



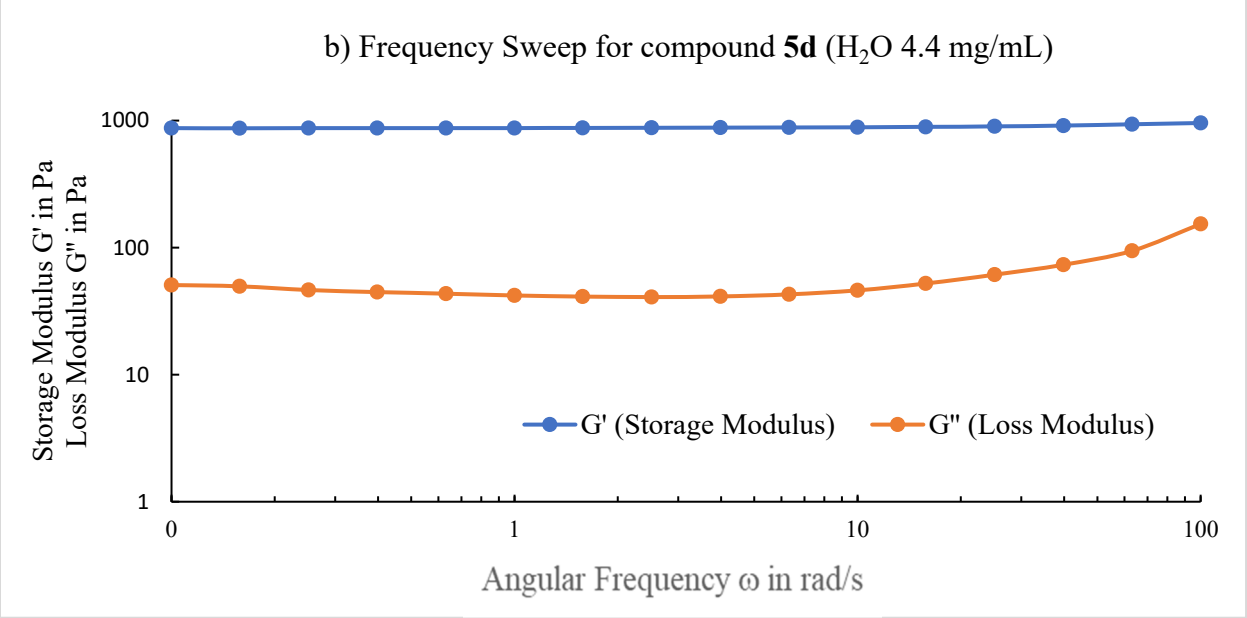
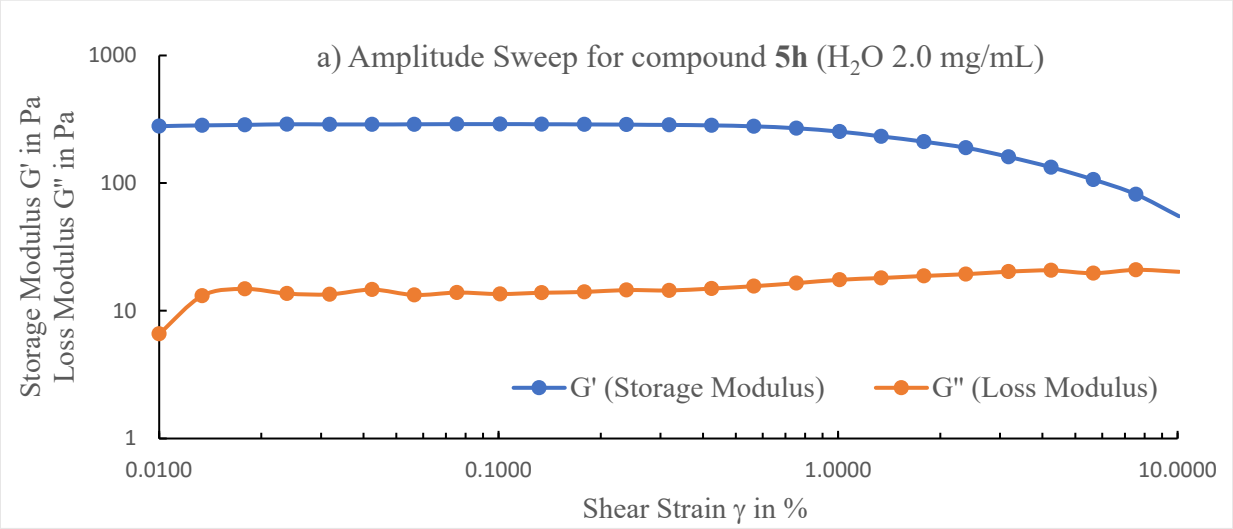


Figure S6. Amplitude sweep (a) and frequency sweep (b) for the hydrogel formed by compound **5d** at 2.2 mg/mL.

4. Rheology data for compound **5h** in water at 2.0 mg/mL



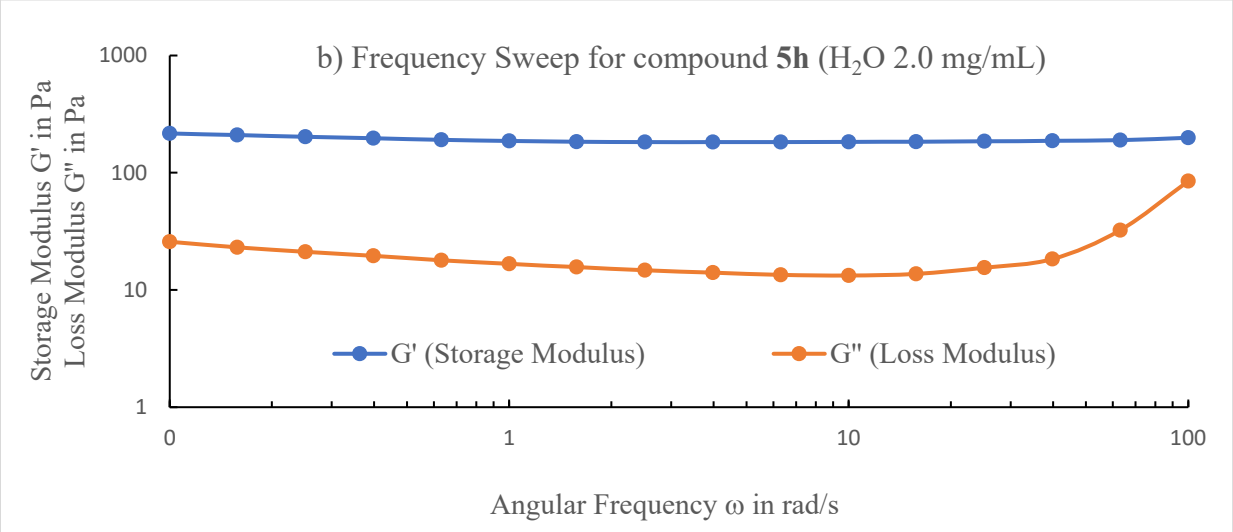
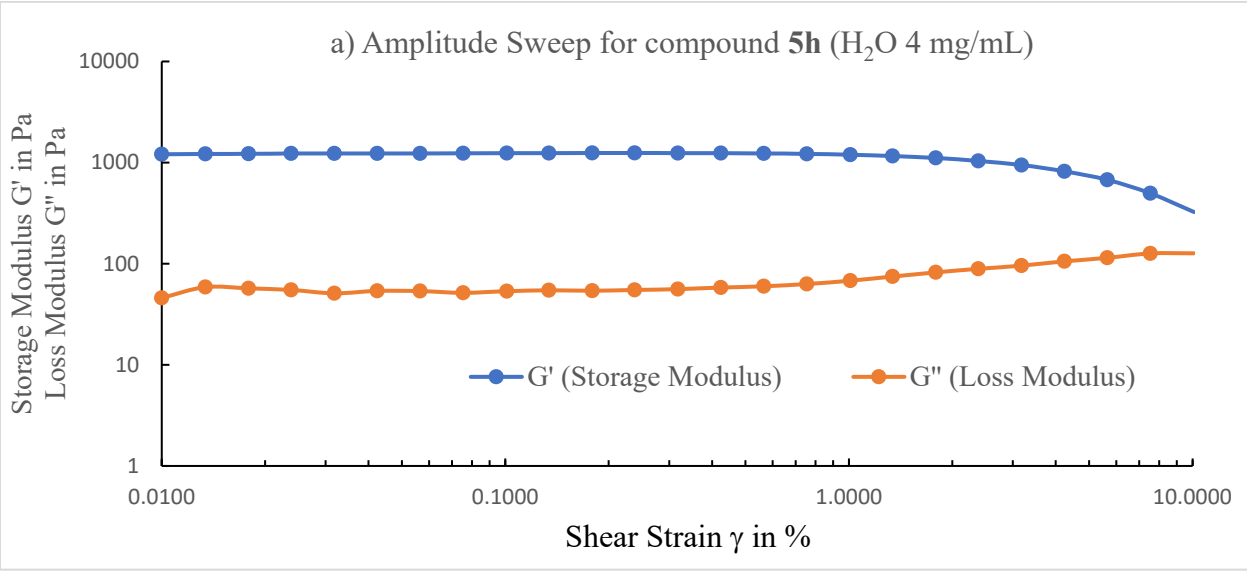


Figure S7. Amplitude sweep (a) and frequency sweep (b) for the hydrogel formed by compound **5h** at 2.0 mg/mL.

5. Rheology data for compound **5h** in water at 4.0 mg/mL



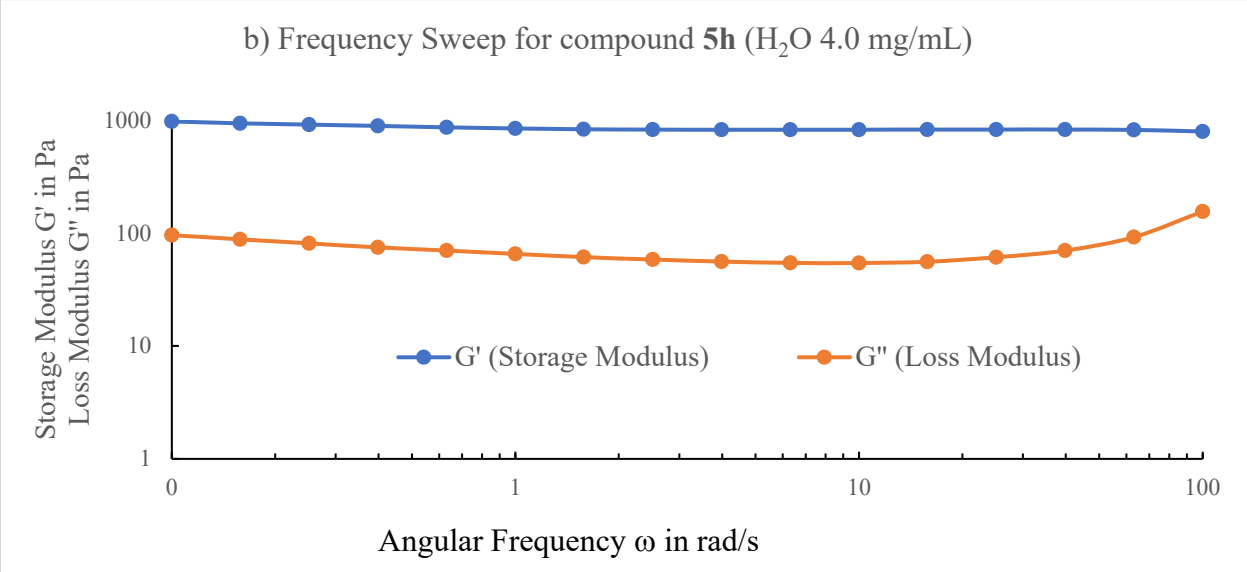
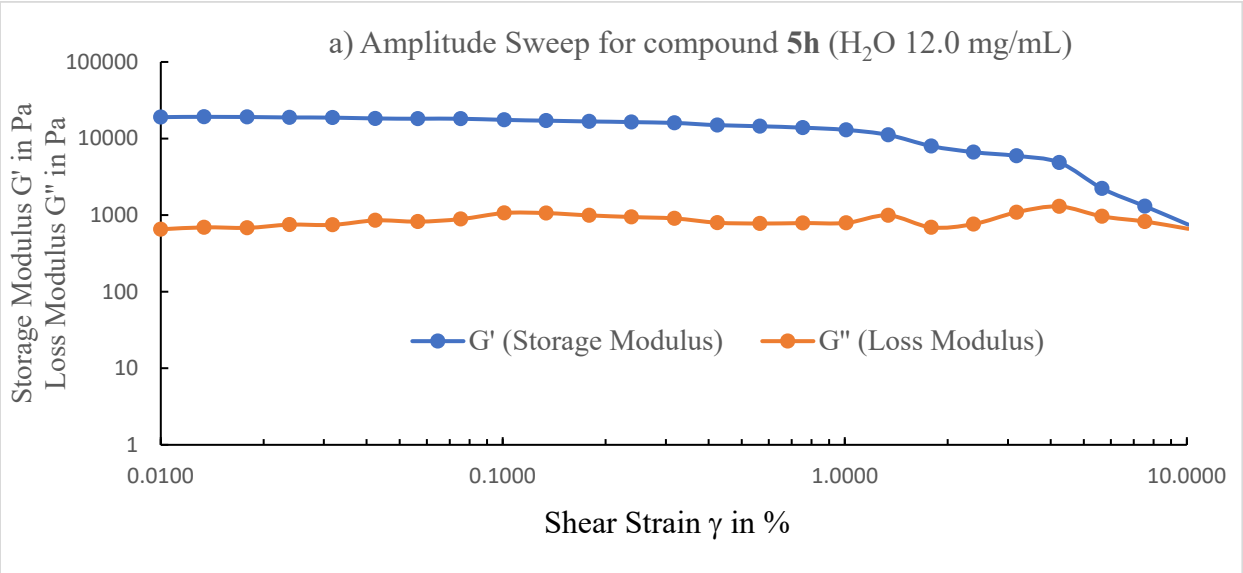


Figure S8. Amplitude sweep (a) and frequency sweep (b) for the hydrogel formed by compound **5h** at 4.0 mg/mL.

6. Rheology data for compound **5h** in water at 12.0 mg/mL



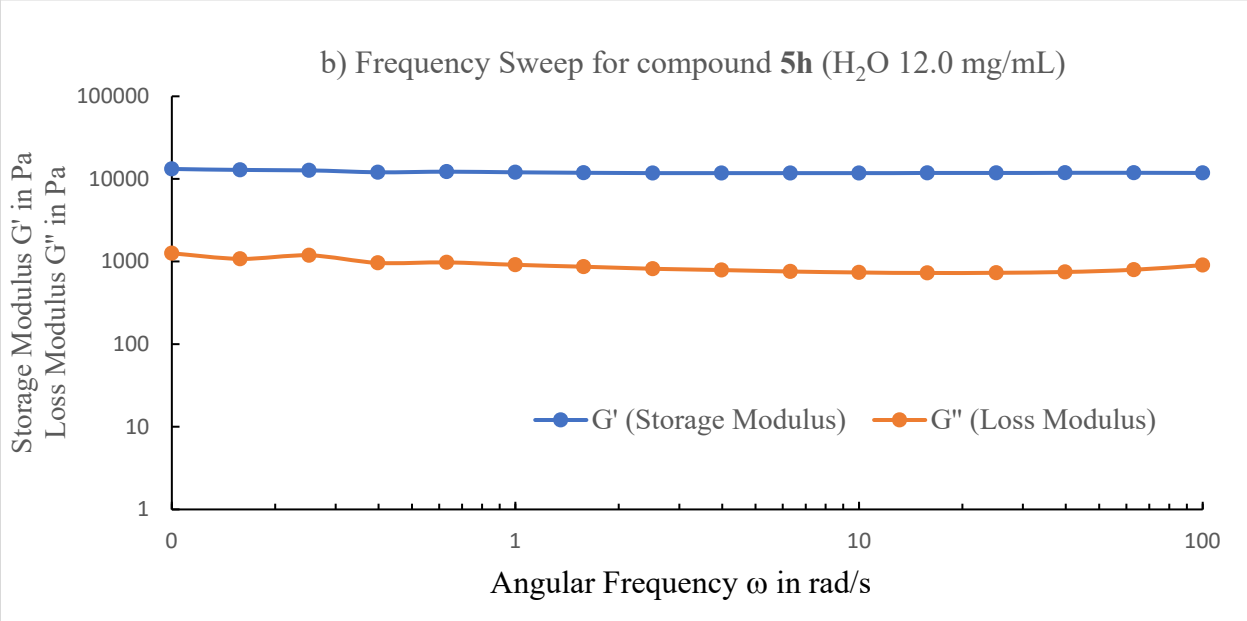


Figure S9. Amplitude sweep (a) and frequency sweep (b) for the hydrogel formed by compound **5h** at 12.0 mg/mL.

Table S1. The G' and G", and ratio of G'/G" for the gel of **5d** in water at 1.1 mg/mL

w [rad/s]	G' (Storage Modulus)	G" (Loss Modulus)	G'/G"
100	174.81	77.28	2.26
63.1	169.72	26.79	6.33
39.8	163.47	14.26	11.46
25.1	159.65	11.17	14.28
15.8	157.07	9.04	17.36
10	154.77	7.72	20.02
6.31	153.35	6.57	23.32
3.98	152.18	5.89	25.83
2.51	151.42	5.39	28.07
1.58	151.03	4.96	30.44
1	150.79	4.78	31.51
0.63	150.77	4.61	32.66
0.39	150.85	4.89	30.79
0.25	150.98	4.84	31.17
0.15	151.11	5.07	29.75
0.1	150.92	5.54	27.21

Table S2. The G' and G", and ratio of G'/G" for the gel of **5d** in water at 2.2 mg/mL

w [rad/s]	G' (Storage Modulus)	G" (Loss Modulus)	G'/G"
100	680.92	148.47	4.58
63.1	638.09	89.33	7.14
39.8	615.01	67.28	9.14
25.1	602.72	57.16	10.54
15.8	596.24	49.82	11.96
10	592	44.59	13.27
6.31	590.28	41.57	14.19
3.98	588.87	39.36	14.96
2.51	588.89	39.21	15.01
1.58	589.17	38.97	15.11
1	590.73	39.52	14.94
0.631	589.84	39.45	14.95
0.398	594.74	39.94	14.88
0.251	595.61	40.57	14.67
0.158	599.28	42.55	14.08
0.1	601.25	44.80	13.41

Table S3. The G' and G", and ratio of G'/G" for the gel of **5d** in water at 4.4 mg/mL

w [rad/s]	G' (Storage Modulus)	G" (Loss Modulus)	G'/G"
100	959.78	153.56	6.25
63.1	935.51	94.54	9.89
39.8	913.76	73.46	12.43
25.1	901.09	61.30	14.69
15.8	892.75	52.23	17.09
10	887.32	46.15	19.22
6.31	883.8	42.87	20.61
3.98	880.98	41.34	21.30
2.51	878.26	40.87	21.48
1.58	876.13	41.23	21.24
1.0	874.67	42.09	20.78
0.63	873.88	43.45	20.10
0.39	873.56	44.74	19.52
0.25	872.96	46.41	18.80
0.15	870.44	49.66	17.52
0.10	872.61	50.80	17.17

Table S4. The G' and G", and ratio of G'/G" for the gel of **5h** in water at 2.0 mg/mL

w [rad/s]	G' (Storage Modulus)	G" (Loss Modulus)	G'/G"
100	198.99	84.79	2.34
63.1	189.72	32.36	5.85
39.8	187.19	18.35	10.19
25.1	185.37	15.48	11.97
15.8	184.13	13.72	13.41
10	183.49	13.28	13.80
6.31	182.78	13.43	13.60
3.98	182.46	14.03	13.00
2.51	182.67	14.71	12.41
1.58	184.09	15.66	11.75
1	186.85	16.68	11.20
0.631	191.07	17.92	10.65
0.398	196.76	19.56	10.05
0.251	202.78	21.16	9.58
0.158	209.51	23.11	9.06
0.1	216.36	25.73	8.40

Table S5. The G' and G", and ratio of G'/G" for the gel of **5h** in water at 4.0 mg/mL

w [rad/s]	G' (Storage Modulus)	G" (Loss Modulus)	G'/G"
100	798.22	155.790	5.12
63.1	823.88	92.535	8.90
39.8	829.81	70.301	11.80
25.1	830.63	61.288	13.55
15.8	829.25	55.95	14.82
10	827.9	54.517	15.19
6.31	827.1	54.568	15.16
3.98	827.16	56.114	14.74
2.51	829.02	58.442	14.18
1.58	835.95	61.479	13.60
1	848.91	65.565	12.95
0.631	868.63	70.257	12.36
0.398	893.15	74.931	11.92
0.251	917.48	81.227	11.29
0.158	943.37	88.398	10.67
0.1	978.25	96.180	10.17

Table S6. The G' and G", and ratio of G'/G" for the gel of **5h** in water at 12.0 mg/mL

w [rad/s]	G' (Storage Modulus)	G" (Loss Modulus)	G'/G"
100	11792	903.62	13.05
63.1	11850	794.33	14.91
39.8	11827	747.37	15.82
25.1	11797	730.54	16.15
15.8	11774	726.15	16.21
10	11747	736.56	15.95
6.31	11738	757.29	15.50
3.98	11730	786.81	14.91
2.51	11764	816.93	14.40
1.58	11842	864.31	13.70
1	12003	912.43	13.15
0.631	12240	975.61	12.54
0.398	12033	962.71	12.49
0.251	12662	1188.50	10.65
0.158	12834	1078.70	11.89
0.1	13188	1257.20	10.48

V. Dye absorption experiments

1. Calibration curve for dyes using UV-Vis spectrometry

1.1 Calibration curve for Rhodamine B

Rhodamine B Base (2 mg, 0.00452 mM) was dissolved in deionized water to prepare a 2.0 mg/L solution, serial dilution was performed to prepare the other solutions: 1.0 mg/L, 0.5 mg/L, and 0.25 mg/L solutions. UV-Vis absorption was taken for all the samples to make standard calibration curve and the absorption at 554 nm (λmax) was used to calculate the calibration curve.

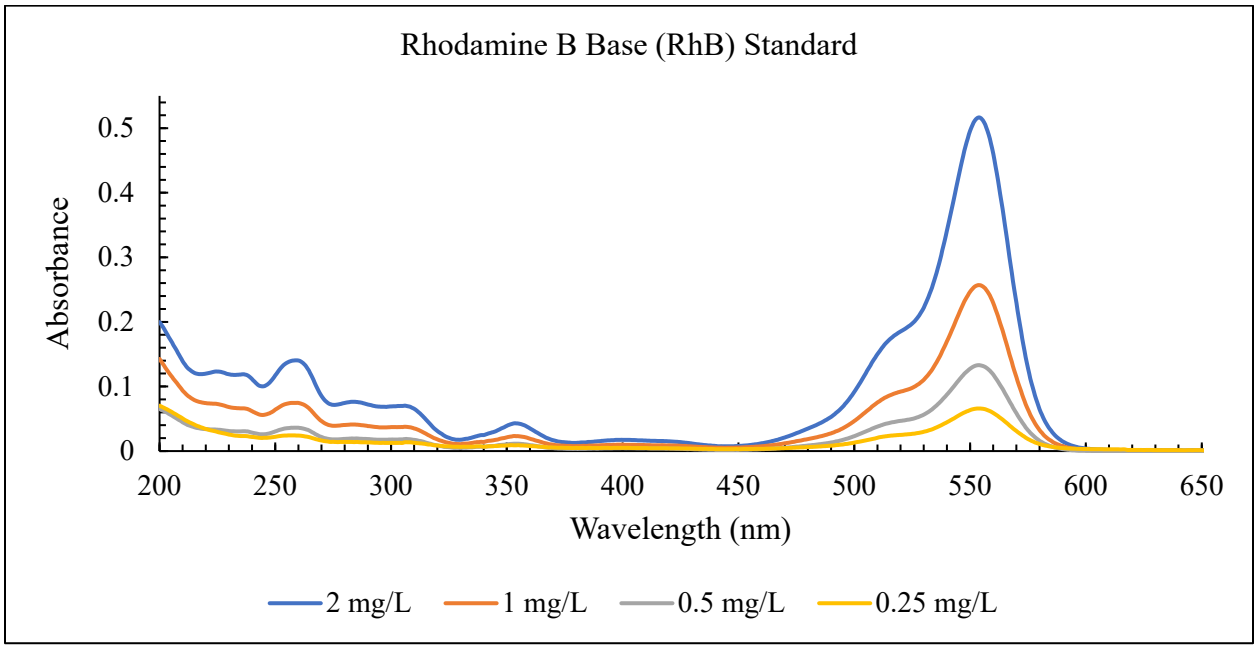


Figure S10. UV-Vis spectra Rhodamine B Base at different concentrations by a serial dilution

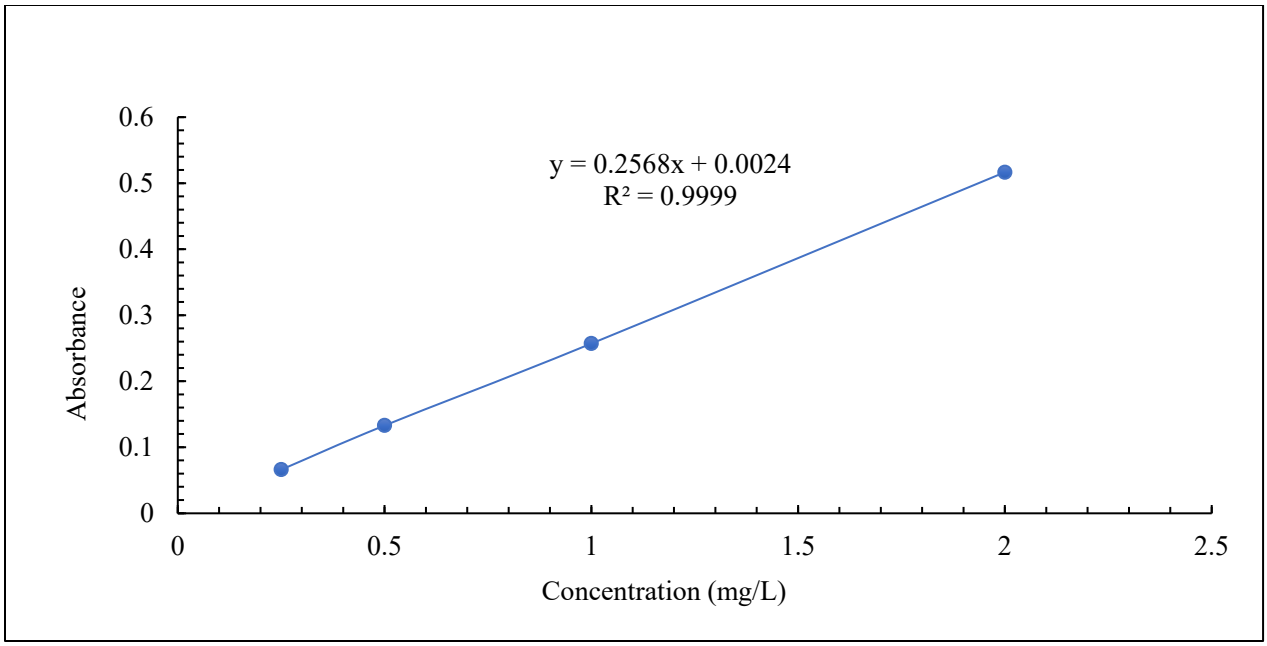


Figure S11. Calibration curve obtained from absorbance reading at 554 nm (λmax)

1.2 Calibration curve for TB

A serial dilution was performed for Toluidine Blue to obtain the standard curve of the dye. An aqueous stock solution was prepared by dissolving Toluidine Blue (10.0 mg) in DI water in a 1 L volumetric flask to yield a concentration of 32.7 µM. This was then serial diluted by transferring 5 mL of the solution to a 10 mL volumetric flask using a volumetric pipette, then diluting it with DI water to obtain solutions with concentrations of 16.35 µM, 8.175 µM, 4.0875 µM, 0.327 µM, 0.0327 µM and 0.000 µM.

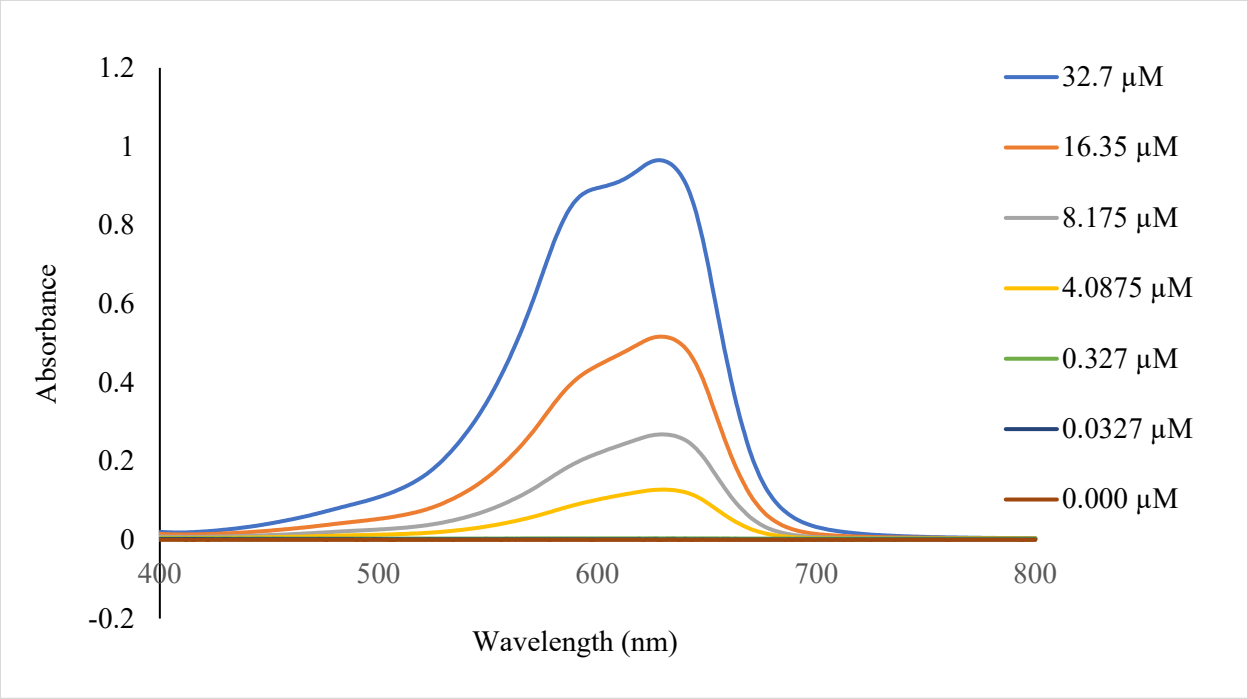


Figure S12. UV-Vis spectra of Toluidine Blue at different concentrations by a serial dilution

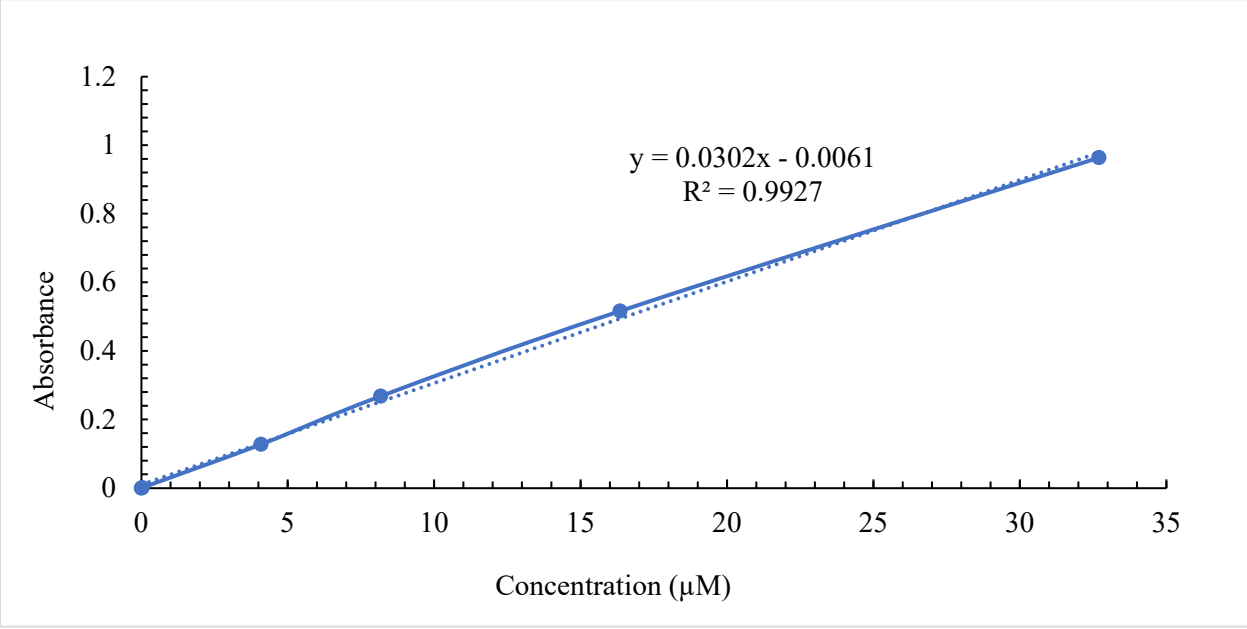


Figure S13. Calibration curve obtained from absorbance reading at 630 nm (λmax)

1.3 Calibration curve for Crystal violet

A serial dilution was performed for crystal violet to obtain the standard curve of the dye. An aqueous stock solution was prepared by dissolving crystal violet (2.0 mg) in DI water in a 100 mL volumetric flask to yield a concentration of 0.0490 mM (20 mg/L). This was then serial diluted by transferring 5 mL of the solution to a 10 mL volumetric flask using a volumetric pipette, then diluting it with DI water to obtain solutions with concentrations of 0.0245 mM (10 mg/L), 0.0123 mM (5 mg/L), 0.00613 mM (2.5 mg/L), 0.00306 mM (1.25 mg/L), and 0.00153 mM (0.625 mg/L).

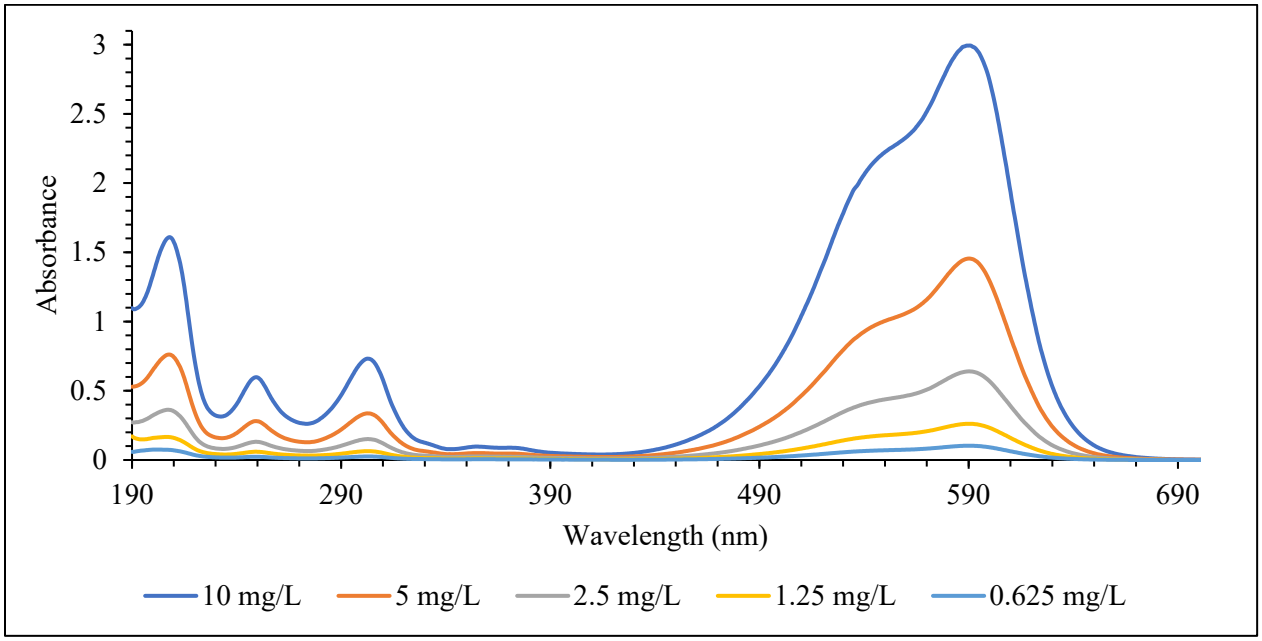


Figure S14. UV-Vis spectra of Crystal Violet at different concentrations by a serial dilution

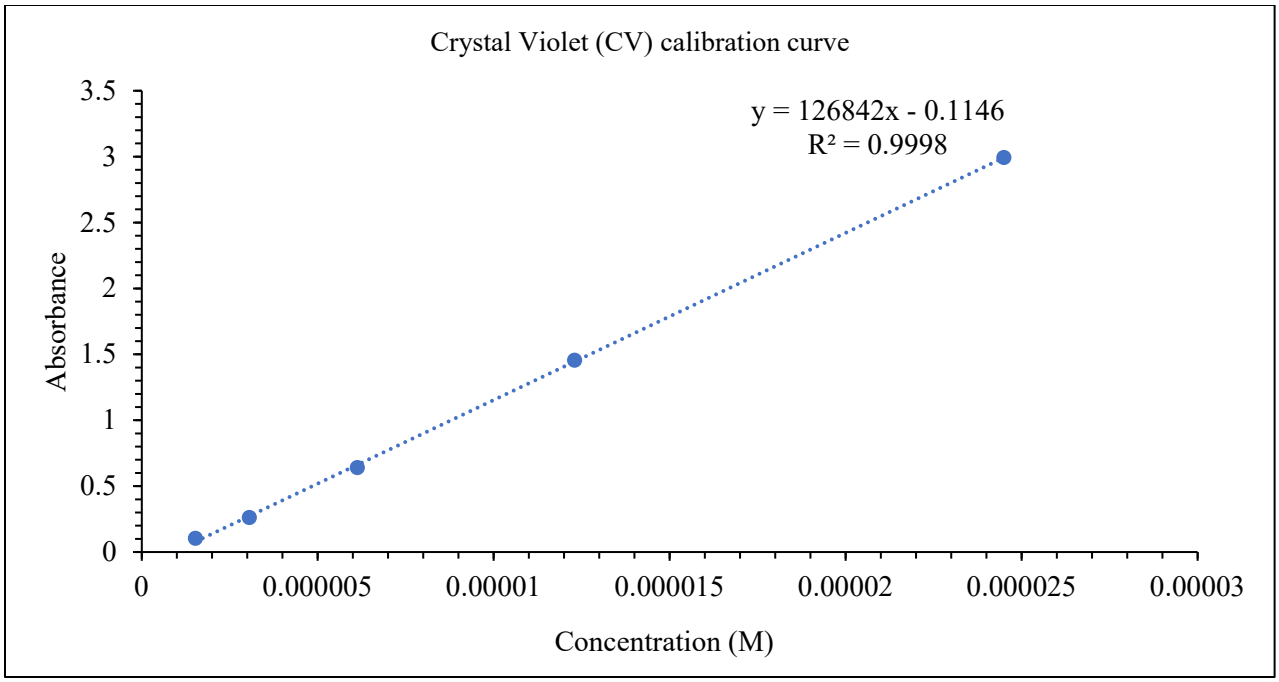


Figure S15. Calibration curve obtained from absorbance reading at 590 nm (λmax).

2. Dye absorption studies using the gels formed by compound **5d**

2.1 Toluidine Blue dye absorption study

The gels formed by compound **5d** in 4.4 mg/mL H_2O were evaluated for the absorption of Toluidine Blue dye. Toluidine Blue (TB) dye 0.1 mL (50 mg/L) was added to 1 mL gel and let settle for half an hour then when the dye was finished passing followed by adding 1 mL water and eluted 1.2 mL liquid was collected and diluted to 2.2 mL. The gel was stable enough to be inverted at the end of the experiment. The gel column removed about 97.9% of the Toluidine Blue dye from the initial solution. The UV-Vis spectra and the gel columns for the study are shown in Figures S16 and S17.

UV absorption λ_{max} (630 nm) = 0.004267

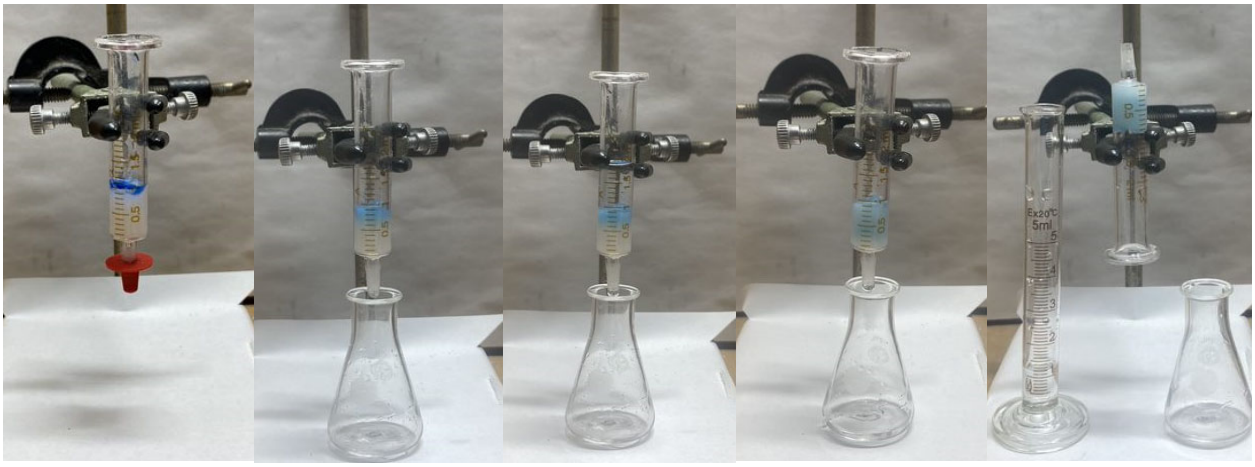
From calibration curve: $y = 0.0302x - 0.0061$

$$0.004267 = 0.0302X - 0.0061 \rightarrow x = \frac{0.004267 + 0.0061}{0.0302} = 0.3432\ \mu M$$

Amount of TB after column: 0.3432 µM × (1 L/1000) × 305.82 × (1 L/1000 mL) × 2.2 mL =0.000105 mg

Original amount of TB added to column: 50.0 mg/L × (1 L/1000 mL) × 0.1 mL= 0.005 mg

Amount of TB removed from the solution: 0.00489 mg, 98%



a b c d e

Figure S16. (a) Gel column of 1.0 mL gel formed by compound **5d** in 4.4 mg/mL H_2O after loading with 0.1 mL TB dye; (b) The gel column after passing 0.1 mL TB dye; (c) 1.0 mL of DI water was added on top of the gel in (b), (d) after passing 1 mL DI water; (e) Inverted gel column with collected aqueous solution.

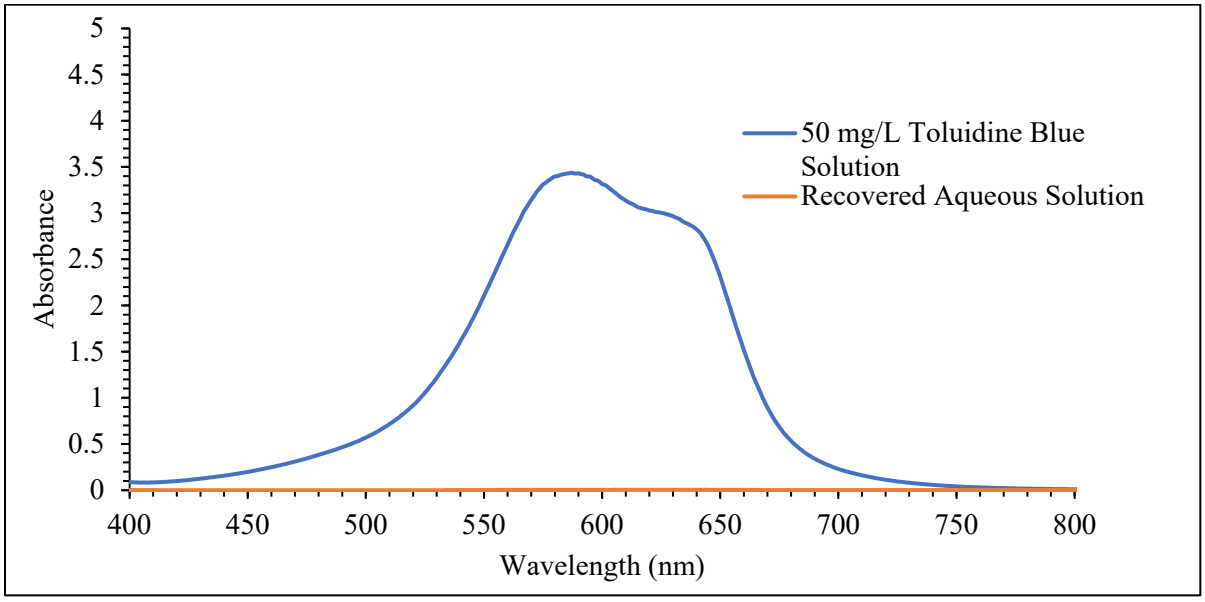


Figure S17. UV-Vis spectra of the initial 50 mg/L TB solution and the collected aqueous solution using the hydrogel compound **5d**, the images are shown in Figures S16.

2.2 Rhodamine B dye absorption study

The gel column (1.0 mL) formed by compound **5d** in 4.4 mg/mL H_2O was evaluated for the absorption of Rhodamine B (RB) dye. RB 0.1 mL (20 mg/L) was added to the gel and let settle for half an hour then the dye solution was allowed to pass through the gel column, after that 1 mL water was added to the gel and eluted, total 1.2 mL liquid was collected. The gel was stable enough to be inverted at the end of the experiment. The gel column removed about 96% of the dye from the initial Rhodamine B solution. The gel columns and UV-Vis spectra and for the study are shown in Figures S18 and S19.

UV absorption for the collected aqueous solution: λ_{max} (554 nm) = 0.0115

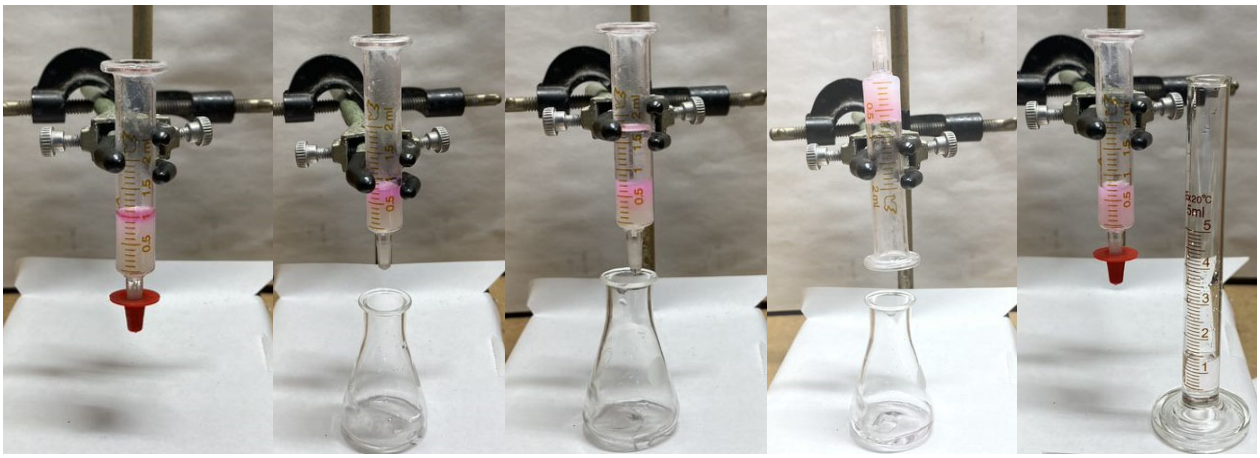
From calibration curve: $y = 0.2568x + 0.0024$

$$0.0115 = 0.2568X + 0.0024 \rightarrow x = (0.0115 - 0.0024)/0.2568 = 0.0357\ mg/L$$

Amount of RB after column: 0.0357 mg/L × (1 L/1000 mL) × 2.2 mL =0.00007857 mg

Original amount of RB added to column: 20 mg/L × (1 L/1000 mL) × 0.1 mL=0.002 mg

Amount of RB removed from the solution: 0.0019 mg, 96%



a b c d e

Figure S18 (a) A 1.0 mL gel column formed by compound **5d** in 4.4 mg/mL H_2O after loading with 0.1 mL Rhodamine B dye; (b) after passing 0.1 mL RB dye; (c) the gel column with added 1.0 mL DI water; (d) inverted gel column after the completion of the experiment; (e) aqueous solution collected from the gel column.

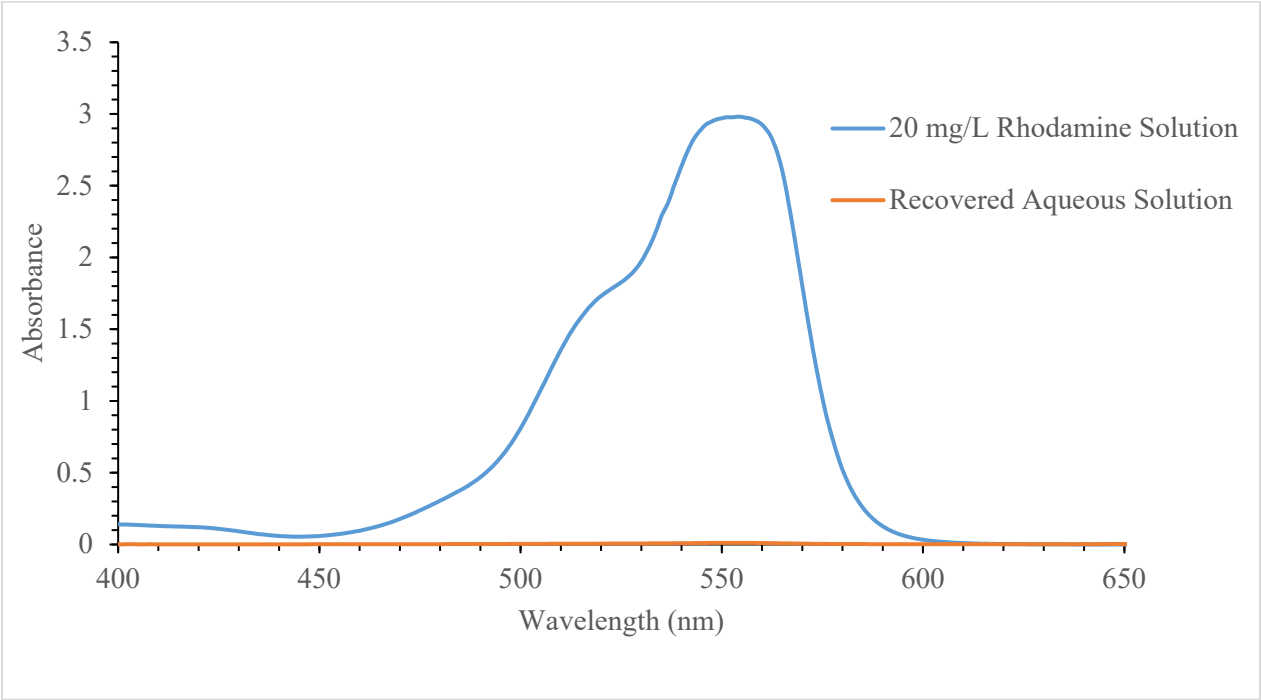


Figure S19. Overlay of UV-Vis spectra of recovered aqueous layer from the study carried out using a gel formed by compound **5d** and the initial Rhodamine B solution.

3. Dye absorption studies using the gels formed by compound **5h**

3.1. Toluidine Blue (TB) dye absorption study

A 2 mL gel formed by compound **5h** in H_2O at 6.0 mg/mL concentration was prepared in a vial and then was heated to form a solution, then transferred to a syringe column with a rubber stopper while hot. The gel formed instantaneously in the syringe, this was left standing for 12 h, (Figure Sx1), then 1.0 mL of toluidine Blue dye (0.005 mg/mL) was added to top of the gel carefully (Fig. 7b) and let the dye solution passing through the column in 30 minutes, the liquid was collected in a small Erlenmeyer flask, after the 1.0 mL dye solution all passed through the gel, another 2.0 mL water was added on top of the gel column and eluted again (Fig. 7c). The eluted liquid was measured in a graduate cylinder and a total of 3.1 mL of liquid was collected. The UV-Vis absorption of the liquid was measured, and this is shown in Figure 8. The gel was stable enough to be inverted at the end of the experiment (Figure d). The absorbance at λ_{max} (630 nm) of Toluidine Blue was measured using measured using a UV-Vis spectrometer. It was estimated that about 82% of the dye was removed from the initial solution. The gel columns and the UV-Vis spectra for the study are shown in Figures S20 and S21.

UV absorption of the collected solution: λ_{max} (630 nm) = 0.0230

From calibration curve: $y = 0.0302x - 0.0061$

$$0.0230 = 0.0302X - 0.0061 \rightarrow x = \frac{0.0230 + 0.0061}{0.0302} = 0.9635\ \mu M$$

Amount of TB after column: 0.9635 μM × (1 L/1000) × 305.82 × (1 L/1000 mL) × 3.1 mL =0.0009134 mg

Original amount of TB added to column: 5.0 mg/L × (1 L/1000 mL) × 1 mL= 0.005 mg

Amount of TB removed from the solution: 0.0040868 mg, 81.7%

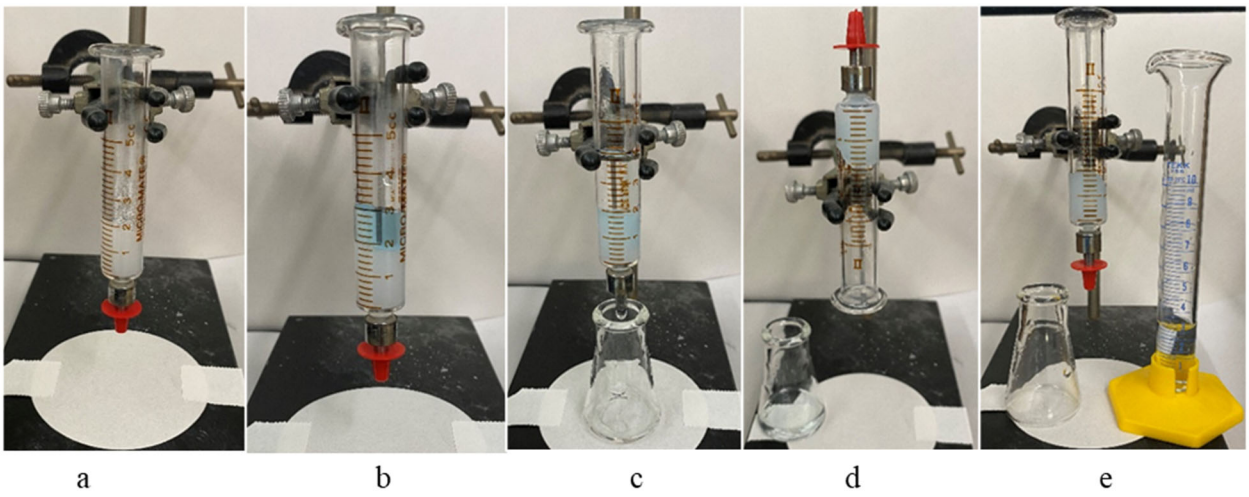


Figure S20. (a) The gel column before the experiment, 2.0 mL gel formed by **5h** in H_2O at 6.0 mg/mL, (b) The gel column after loading with 1.0 mL TB dye; (c) Washing the column with 2.0 mL of DI water; (d) Inverted gel column after the completion of the experiment; (e) Aqueous solution collected from the gel column.

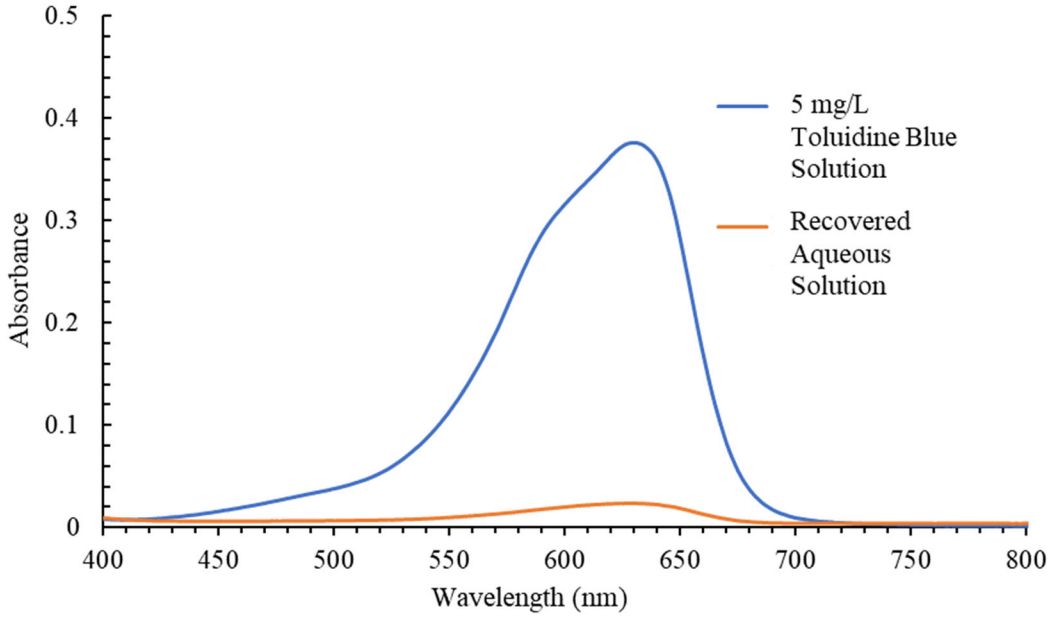


Figure S21. UV-Vis spectra of the collected aqueous solution and the initial toluidine blue solution loaded to the gel column.

3.2. Rhodamine B dye absorption study

A 2.0 mL gel formed by compound **5h** in 6 mg/mL H_2O was prepared similarly as described above. This was evaluated for the absorption of Rhodamine B (RB) dye. A 1.0 mL RB dye solution (2 mg/L) was added on to the gel and let settle for half an hour, then the stopper was opened, and the dye solution passed through the gel column, after the dye finished passing through the column, 2.0 mL water was added to the gel column and eluted. The total collected liquid was 3.2 mL. The gel was stable enough to be inverted at the end of the experiment. The absorbance of RB at λ_{max} (554 nm) was measured using UV-Vis spectrometer. The gel column removed about 76% of the dye from the initial solution. The gel columns and UV-Vis spectra and for the study are shown in Figures S22 and S23.

Calculation for the dye removal:

UV absorption of the collected solutions: λ_{max} (554 nm) = 0.0397

From calibration curve: $y = 0.2568x + 0.0026$

$$0.0397 = 0.2568X + 0.0026 \rightarrow x = (0.0397 - 0.0026)/0.2568 = 0.14447\ mg/L$$

Amount of RB after column: 0.2176 mg/L × (1 L/1000 mL) × 3.2 mL =0.000462 mg

Original amount of RB added to column: 2.0 mg/L × (1 L/1000 mL) × 1 mL=0.002 mg

Amount of RB removed from the solution: 0.001538 mg, 76%

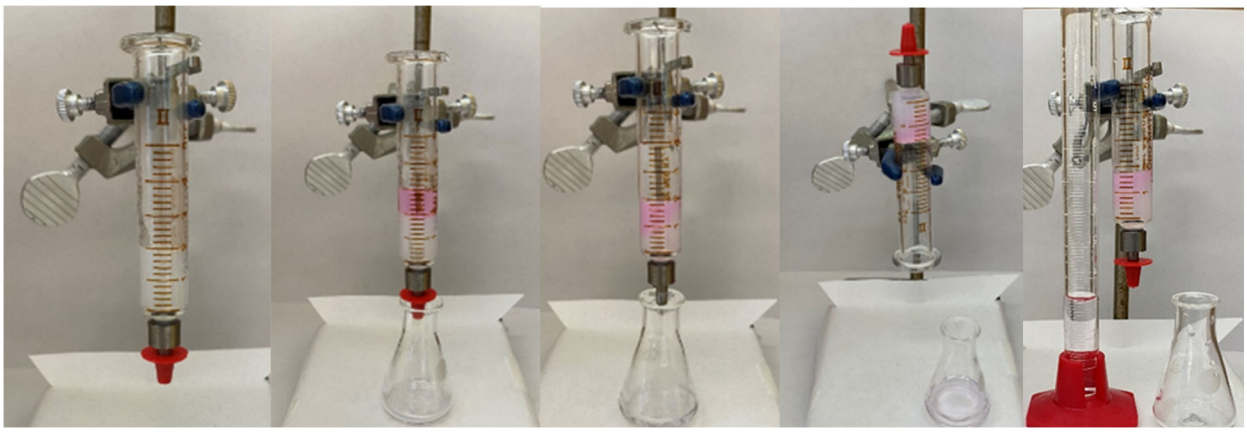


Figure S22. (a) The gel column before the experiment, the 2.0 mL gel was formed by compound **5h** in water at 6 mg/mL concentration; (b) the gel column after loading with 1 mL RB dye; (c) 2.0 mL DI water was added to the gel column after RB dye elution; (d) Inverted gel column after the completion of the experiment; (e) Aqueous solution collected from the gel column.

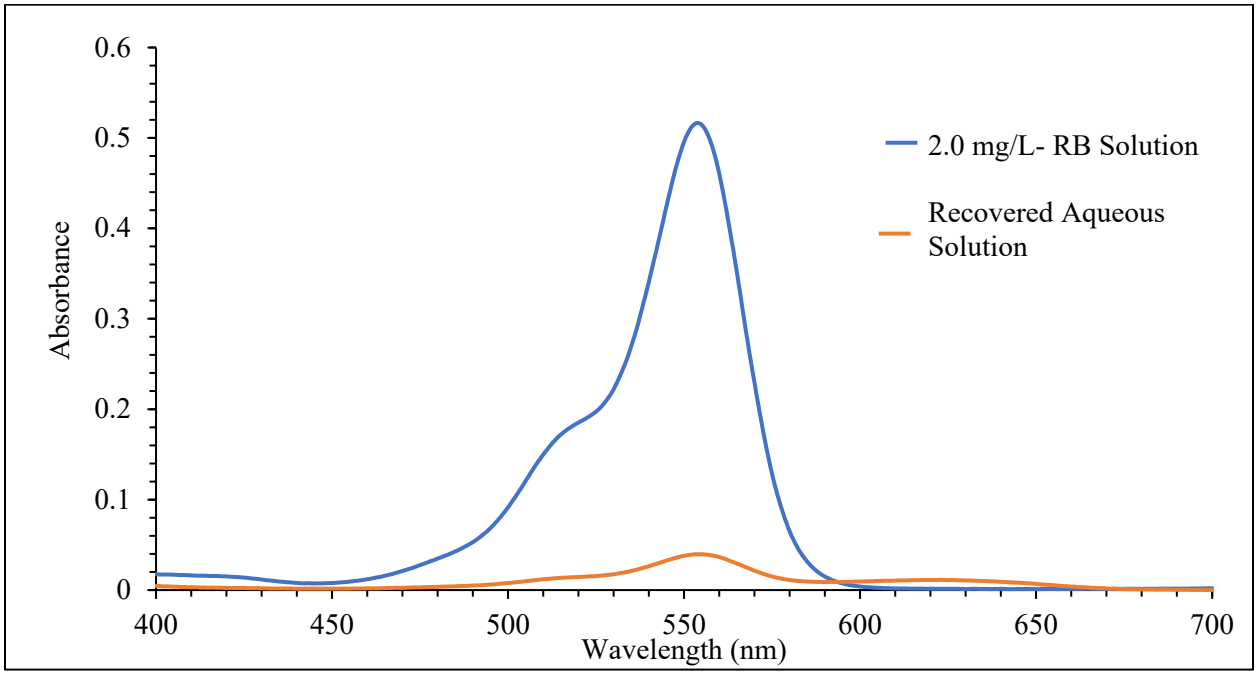


Figure S23. Overlay of UV-Vis spectra of recovered aqueous solution from the study carried out using the gel formed by compound **5h** and the initial 2 mg/L Rhodamine B solution.

3.3. Mixed dye absorption study

The 1.0 mL gel column (Figure 6) formed by compound **5h** in H_2O (8.0 mg/mL) was evaluated for the absorption of Rhodamine B and Toluidine Blue dye mixture. The mixture of 0.5 mL RB (2.0 mg/mL) and 0.5 mL TB (5.0 mg/mL) solutions was added to the gel and let settle for half an hour. The dye solution was eluted from the gel column and after the mixture finished eluting, 1.0 mL water was added to the gel column and eluted again, a total 2.0 mL liquid was collected. The gel was stable enough to be inverted at the end of the experiment. The UV-Vis spectra of the dye solutions and the collected aqueous solution are shown in Figure S24 and Figure 7. The gel column successfully removed, 79% of the Rhodamine B dye and 82%.

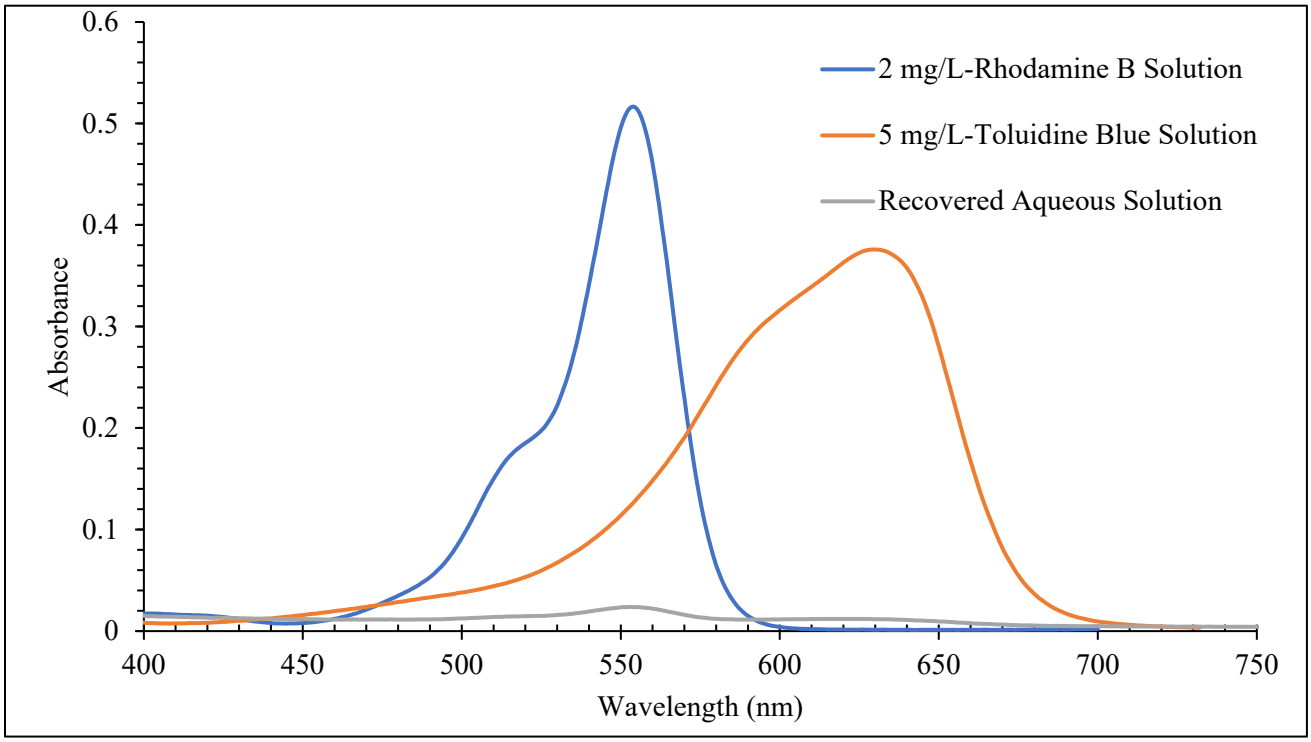


Figure S24. Overlay of UV-Vis spectra of collected aqueous solution from the study carried out using a gel formed by compound **5h** and the initial 2.0 mg/L Rhodamine B and 5.0 mg/L Toluidine Blue solution.

Calculation of the dyes absorbed:

The UV absorptions of the collected aqueous solution versus the initial dye solutions were used.

1. *Rhodamine B dye absorption*

UV absorption λ_{max} (554 nm) = 0.0237

From calibration curve: $y = 0.2568x + 0.0026$

$$0.0237 = 0.2568X + 0.0026 \rightarrow x = (0.0237 - 0.0026)/0.2568 = 0.0821\ mg/L$$

Amount of RB after column: 0.0821 mg/L × (1 L/1000 mL) × 2.5 mL =0.00021 mg

Original amount of RB added to column: 2.0 mg/L × (1 L/1000 mL) × 0.5 mL=0.001 mg

Amount of RB removed from the solution: 0.00079 mg, 79%

2. *Toluidine blue dye absorption*

UV absorption λ_{max} (630 nm) = 0.0117

From calibration curve: $y = 0.0302x - 0.0061$

$$0.0117 = 0.0302X - 0.0061 \rightarrow x = (0.0117 + 0.0061)/0.0302 = 0.5894\ \mu M$$

Amount of TB after column: $0.5894\ \mu M$ × (1/1000) × (1 L/1000 mL) × 305.82 × 2.5 mL = 0.000450 mg

Original amount of TB added to column: 5.0 mg/L × (1 L/1000 mL) × 0.5 mL=0.0025 mg

Amount of TB removed from the solution: 0.00204 mg, 82%

3.4 Dye absorption for three different dyes sequentially using the same gel column.

As shown in Figure S25, a 1.0 mL hydrogel formed by compound **5h** in 8.0 mg/mL H_2O was prepared in a 2 mL glass syringe with a stopper plug. This gel was evaluated for the absorption of three different dyes sequentially, Crystal Violet (CV), Rhodamine B (RB), and Toluidine Blue (TB) dyes. First, 0.5 mL of Crystal Violet (5.0 mg/L) was added to the gel and was left standing for 0.5 h and the plug was removed to allow the dye solution to pass through the gel column, after the dye solutions finished eluting, 1.0 mL water was added on top of the gel, then the liquid passing through the column was collected. The UV-Vis spectra of the dye solution and the collected

aqueous solution are shown in Figure S26. The same procedure was repeated for Rhodamine B (2.0 mg/L) followed by Toluidine Blue (5.0 mg/L). The gel was stable enough to be inverted at the end of the experiment. The UV-Vis absorption for the dyes were used for the calculation of the estimated amount being removed by the gel columns for each dye. The details are shown below. The gel columns and UV-Vis spectra for RB removal and TB removal are shown in Figures S27-S30. Using a calibration curve of the dye's solution, we estimate that the gel column removed 58% Crystal Violet, 56% of Rhodamine B, and 82% of Toluidine Blue.

Crystal Violet dye removal:

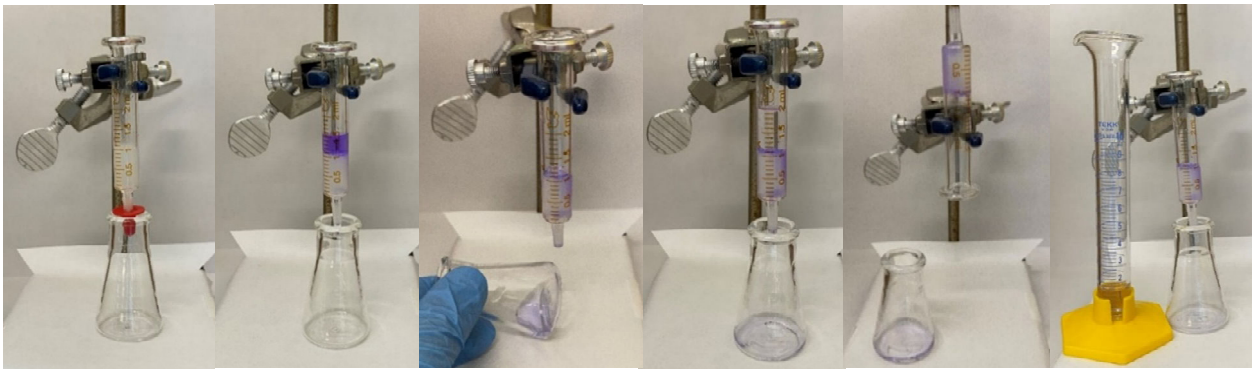
From calibration curve: $y = 126842x - 0.1146$

$$0.0523 = 126842X - 0.1146 \rightarrow x = (0.0523 + 0.1146)/126842 = 0.000001316\ M$$

Amount of CV after column: 0.000001316 M × (1 L/1000 mL) × 2 mL × 407.979 × 1000 mg =0.001074 mg

Original amount of CV added to column: 0.005 mg/mL × 0.5 mL=0.0025 mg

Amount of CV removed from the solution: 0.001426 mg, 58%



a b c d e f

Figure S25. (a) The gel column of 1.0 mL hydrogel formed by compound **5h** at 8.0 mg/mL; (b) 0.5 mL of Crystal Violet solution was added; (c) the gel column after CV dye elution; (d) washing the column with 1 mL of DI water; (e) inverted gel column after the completion of the experiment; (f) aqueous solution collected from the gel column.

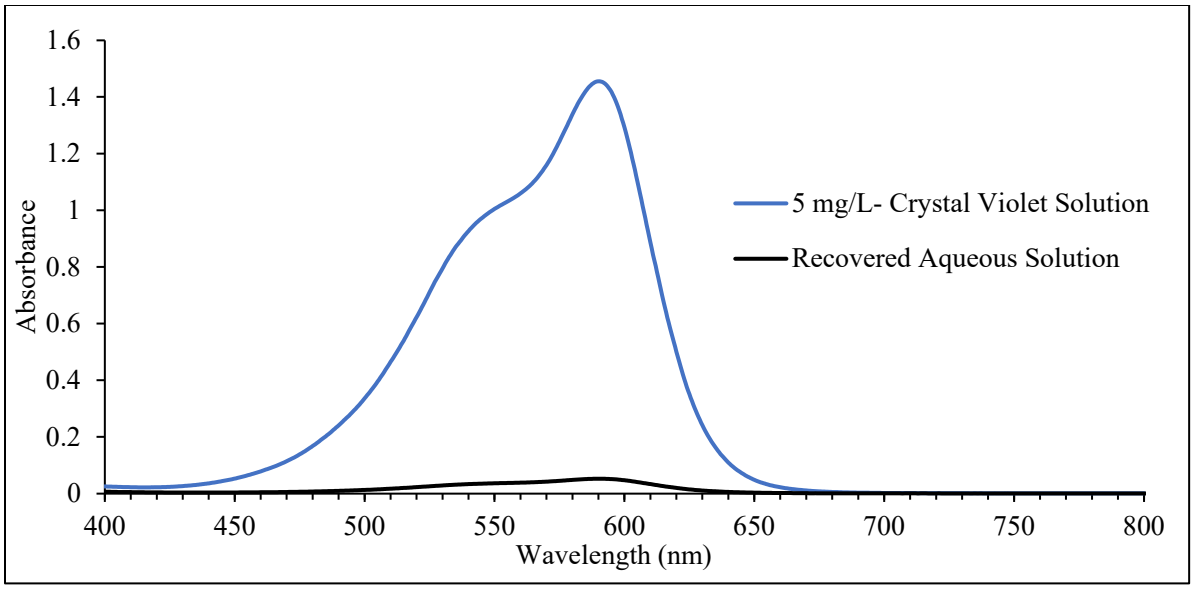


Figure S26. Overlay of UV-Vis spectra of collected aqueous solution in Figure S25 and the initial 5.0 mg/L Crystal Violet solution.

The above gel column was then reused for rhodamine B dye removal by similar procedure as shown in Figure S27 and 28. A 0.5 mL of Rhodamine B (2 mg/L) solution was added to the gel and was left standing for 0.5 h and the plug was removed to allow the dye solution to pass through the gel column, after the dye solutions finished eluting, then 1.0 mL water was added on top of the gel, then the liquid passing through the column was collected.

The estimated amount of dye removed were calculated:

UV absorption λ_{max} (554 nm) = 0.0585

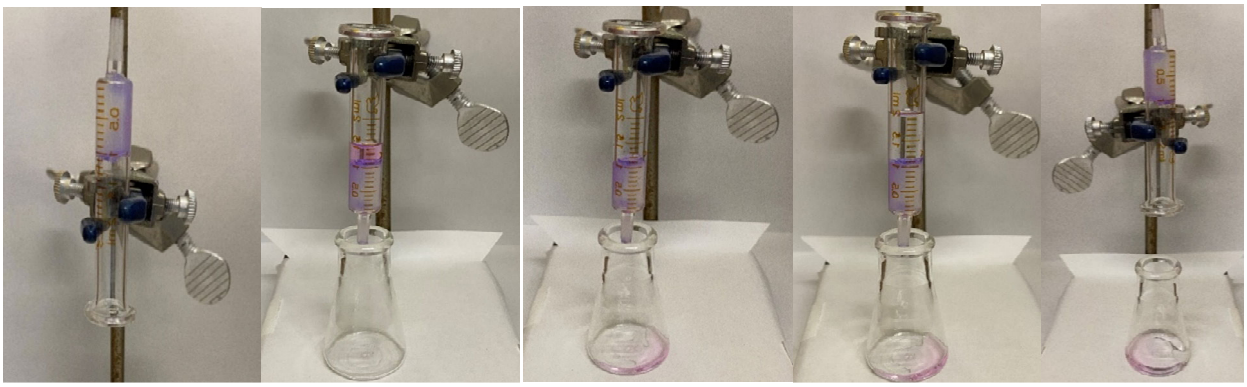
From calibration curve: $y = 0.2568x + 0.0026$

$$0.0585 = 0.2568X + 0.0026 \rightarrow x = (0.0585 - 0.0026)/0.2568 = 0.2176\ mg/L$$

Amount of Rhodamine B after column: 0.2176 mg/L × (1 L/1000 mL) × 2 mL =0.000435 mg

Original amount of Rhodamine B added to column: 2.0 mg/L × (1 L/1000 mL) × 0.5 mL=0.001 mg

Amount of Rhodamine B removed from the solution: 0.00056 mg, 56%



a b c d e

Figure S27. (a) The gel column (compound **5h** at 8.0 mg/mL after CV elution) before Rhodamine B experiment; (b) after loading with 0.5 mL of Rhodamine B; (c) after passing dye; (d) the gel column with 1 mL of DI water; (e) inverted gel column after the completion of the experiment with aqueous solution collected from the gel column.

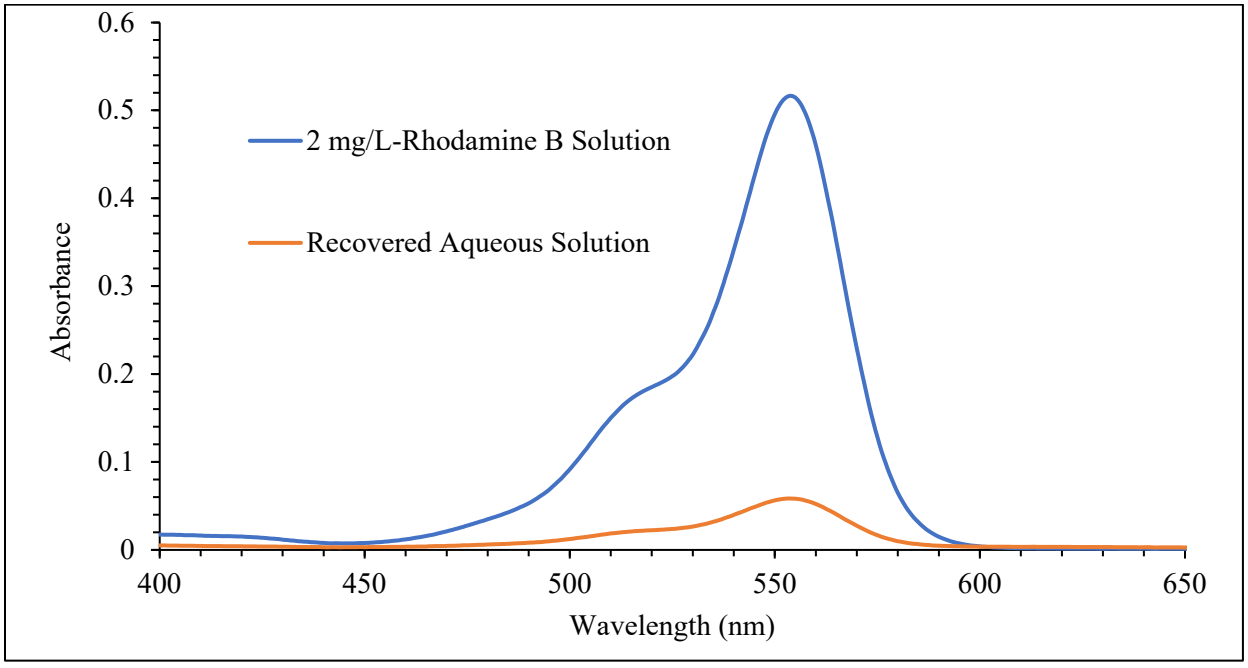


Figure S28. Overlay of UV-Vis spectra of recovered aqueous solution and the initial 2.0 mg/L Rhodamine B solution.

The above gel column was then reused again for Toluidine blue dye removal as shown in Figures S29 and S30. A 0.5 mL of Toluidine blue solution (5.0 mg/L) was added to the gel and was left standing for 0.5 h and the plug was removed to allow the dye solution to pass through the gel column, after the dye solutions finished eluting, then 1.0 mL water was added on top of the gel, then the liquid passing through the column was collected. The estimated amount of dye removed are calculated:

UV absorption λ_{max} (630 nm) = 0.0166

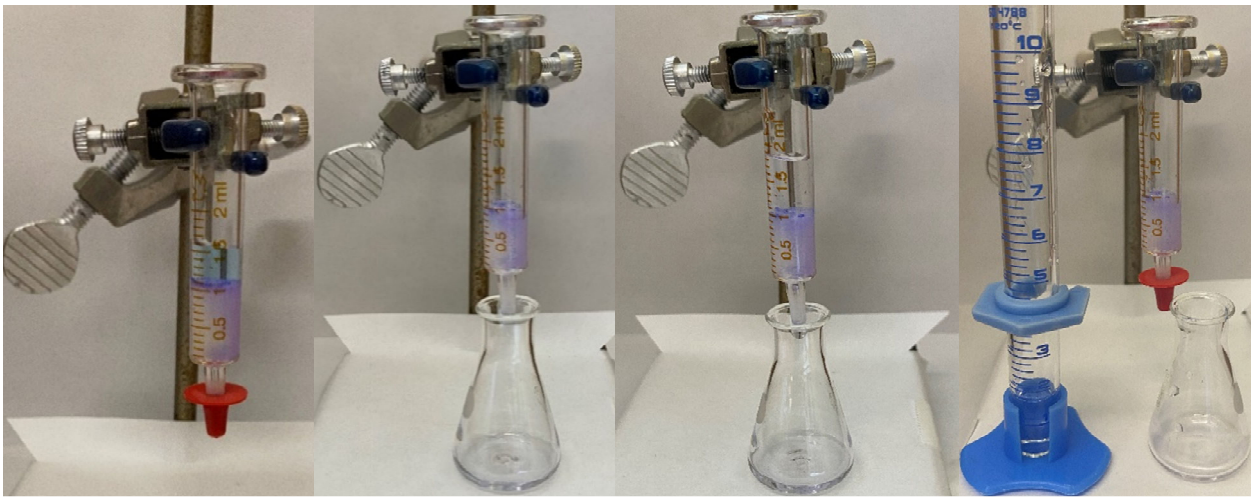
From calibration curve: $y = 0.0302x - 0.0061$

$$0.0166 = 0.0302X - 0.0061 \rightarrow x = (0.0166 + 0.0061)/0.0302 = 0.7516\ \mu M$$

Amount of TB after column: 0.7516 μM × (1 /1000) × (1 L/1000 mL) × 305.82 × 2 mL =0.00045 mg

Original amount of TB added to column: 5.0 mg/L × (1 L/1000 mL) × 0.5 mL=0.0025 mg

Amount of TB removed from the solution: 0.00205 mg, 82%



a b c d

Figure S29. (a) The gel column (compound **5h** at 8.0 mg/mL after RB elution) loaded with 0.5 mL of Toluidine Blue; (b) the gel column after passing dye; (c) washing the column with 1 mL of DI water; (d) the gel column after the completion of the experiment with aqueous solution collected from the gel column.

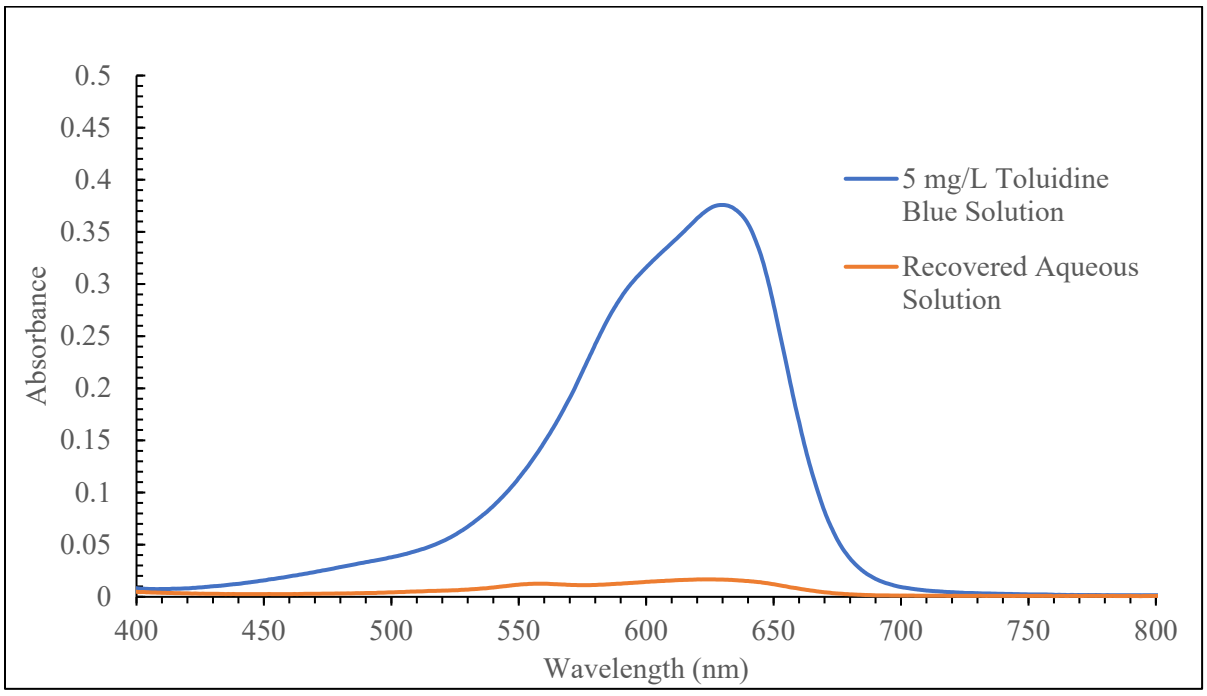


Figure S30. Overlay of UV-Vis spectra of recovered aqueous solution and the initial Toluidine Blue solution.

VI. ^{1}H and ^{13}C NMR spectra of intermediates compounds 5a-5k, 7h, 7i, and 7k

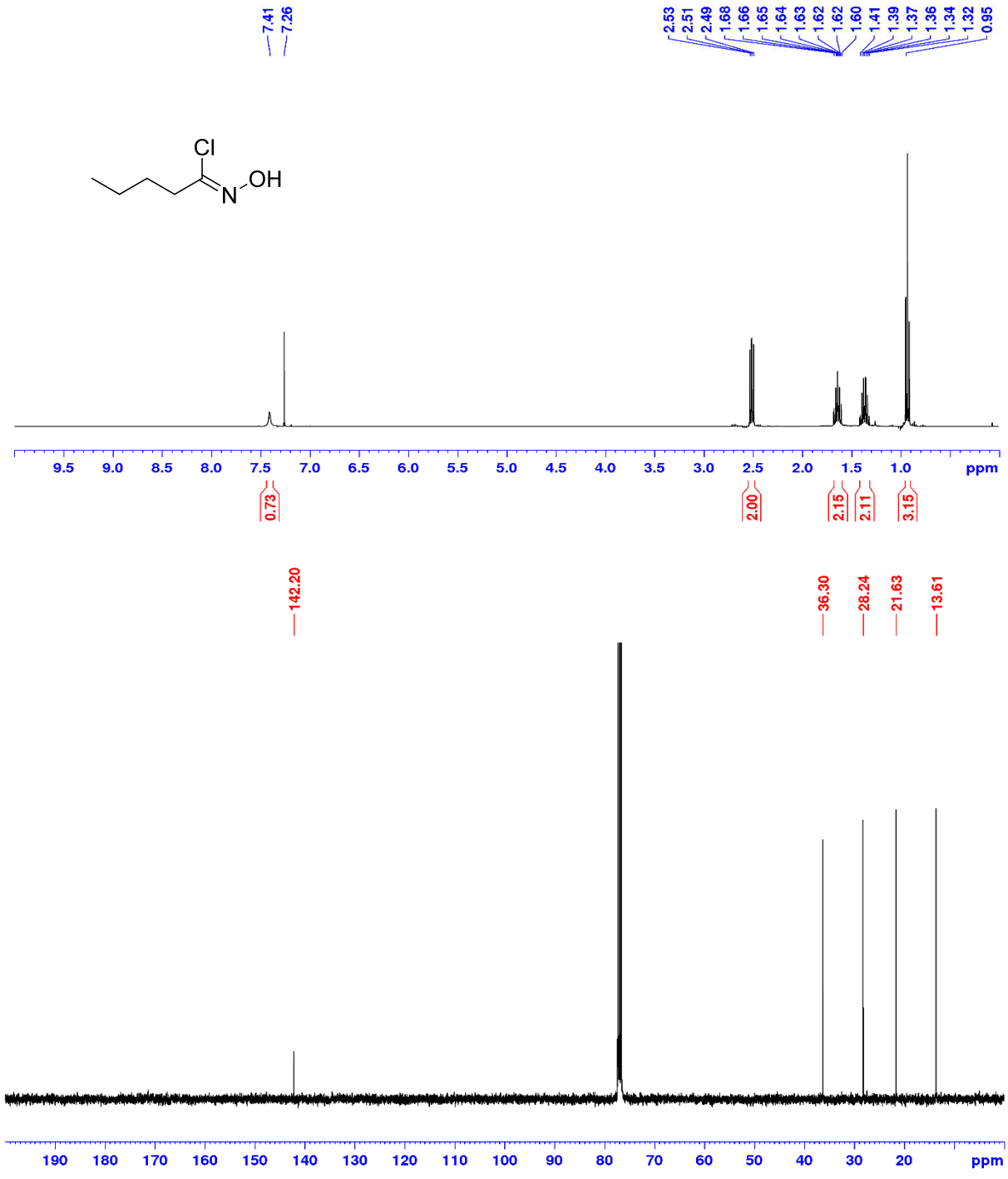


Figure S31. ^{1}H and ^{13}C NMR spectra of compound **3a** in $CDCl_3$

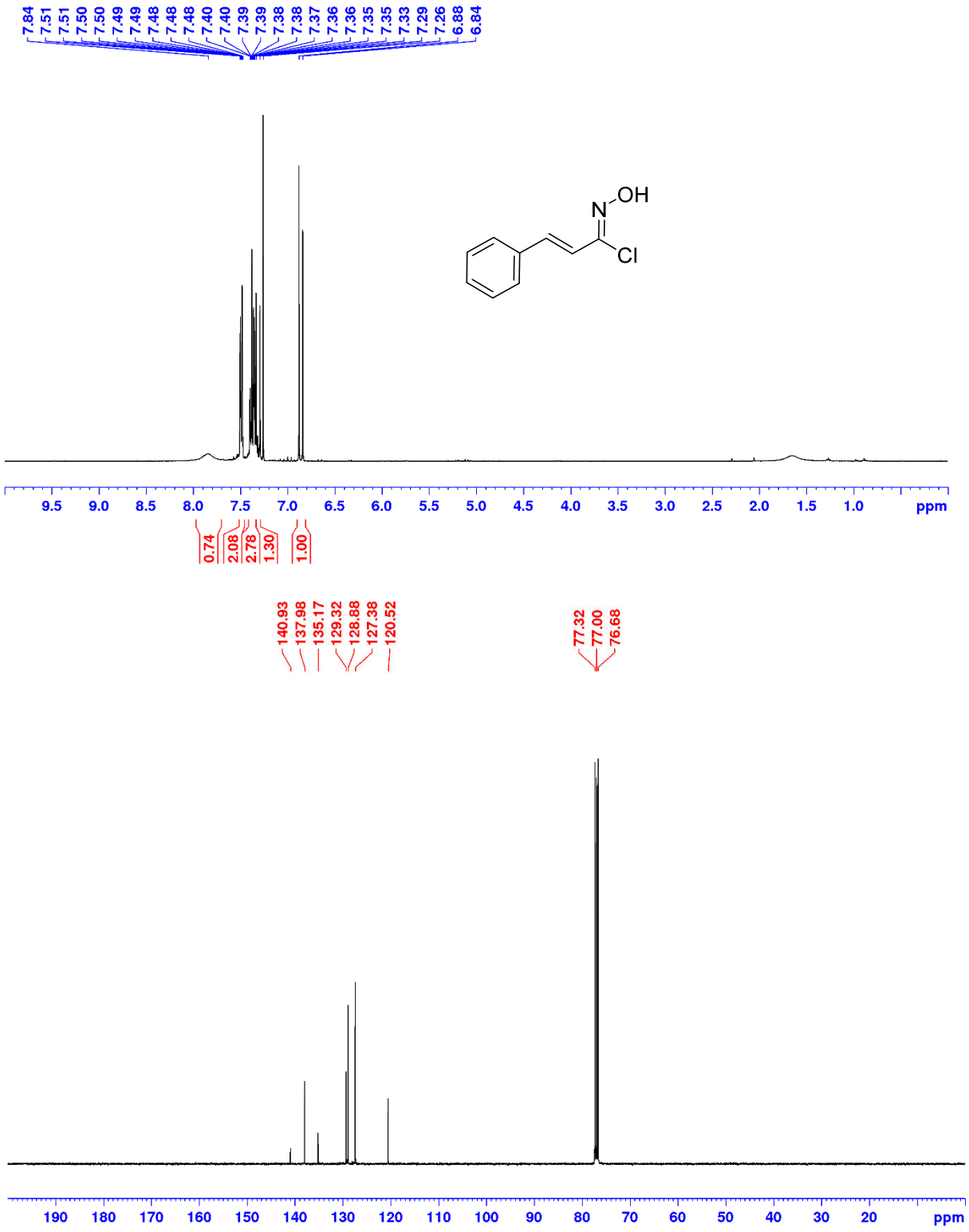


Figure S32. ^{1}H and ^{13}C NMR spectra of compound **3b** in $CDCl_3$

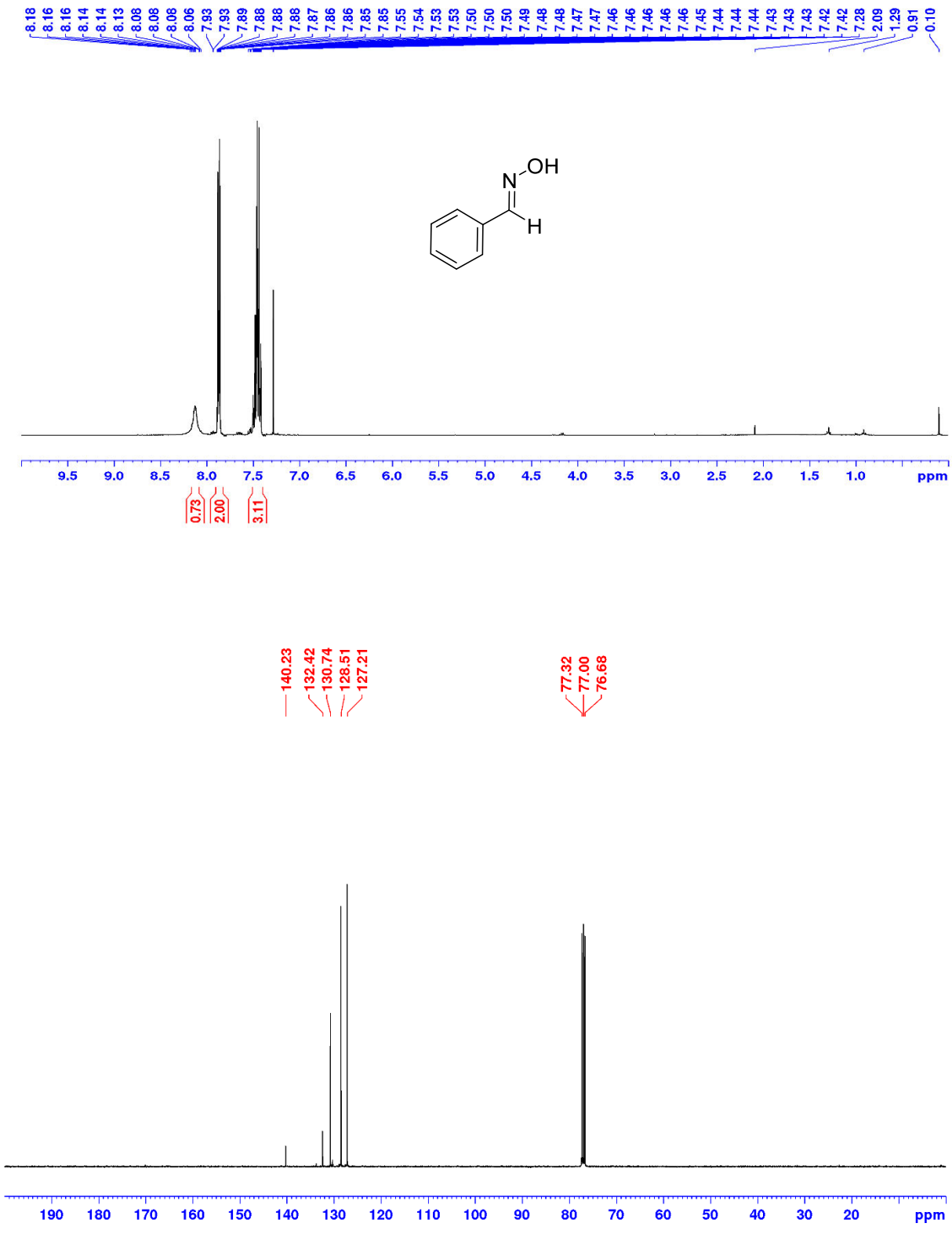


Figure S33. ^{1}H and ^{13}C of compound **3c** in $CDCl_3$

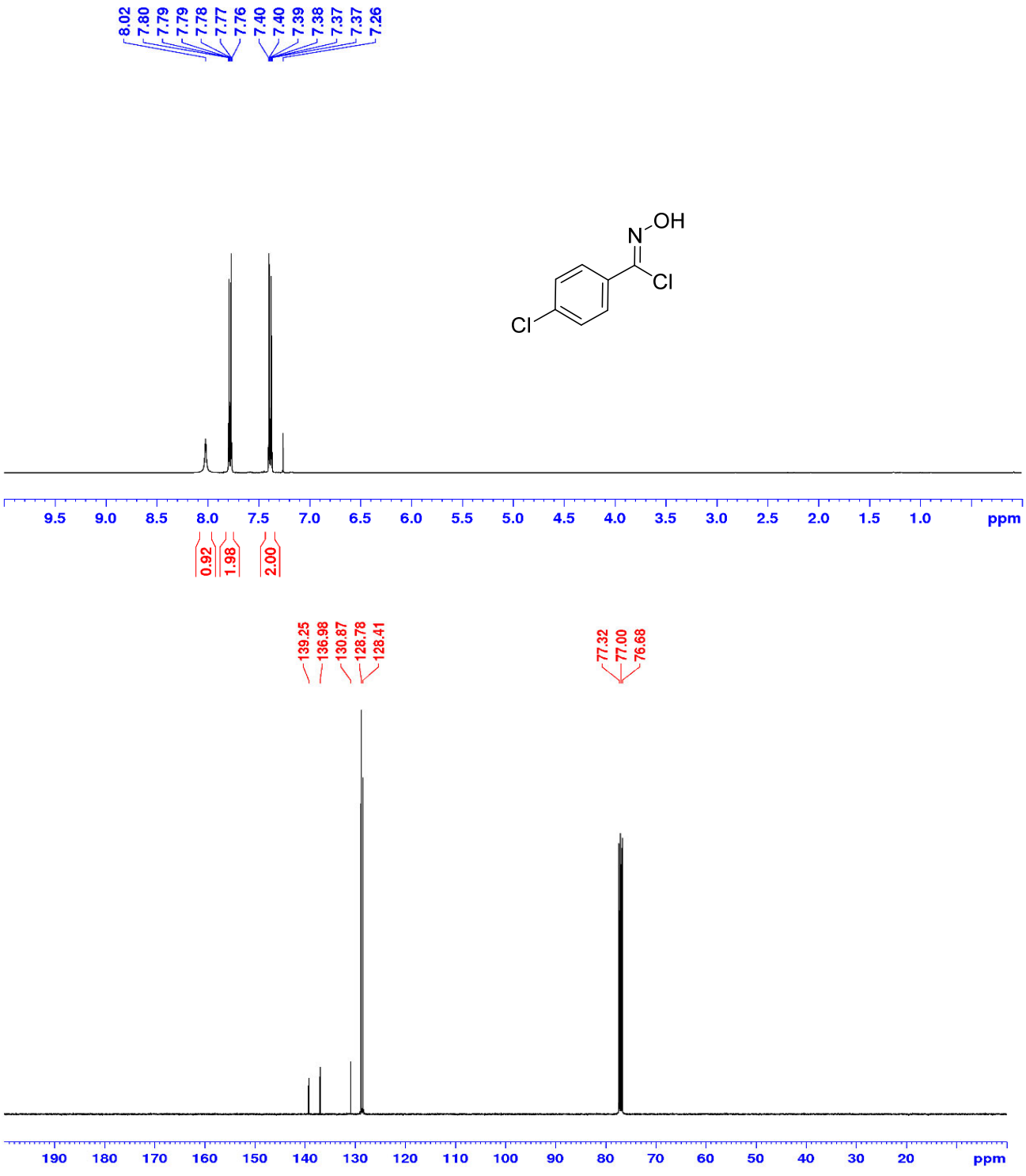


Figure S34. ^{1}H and ^{13}C NMR spectra of compound **3d** in $CDCl_3$

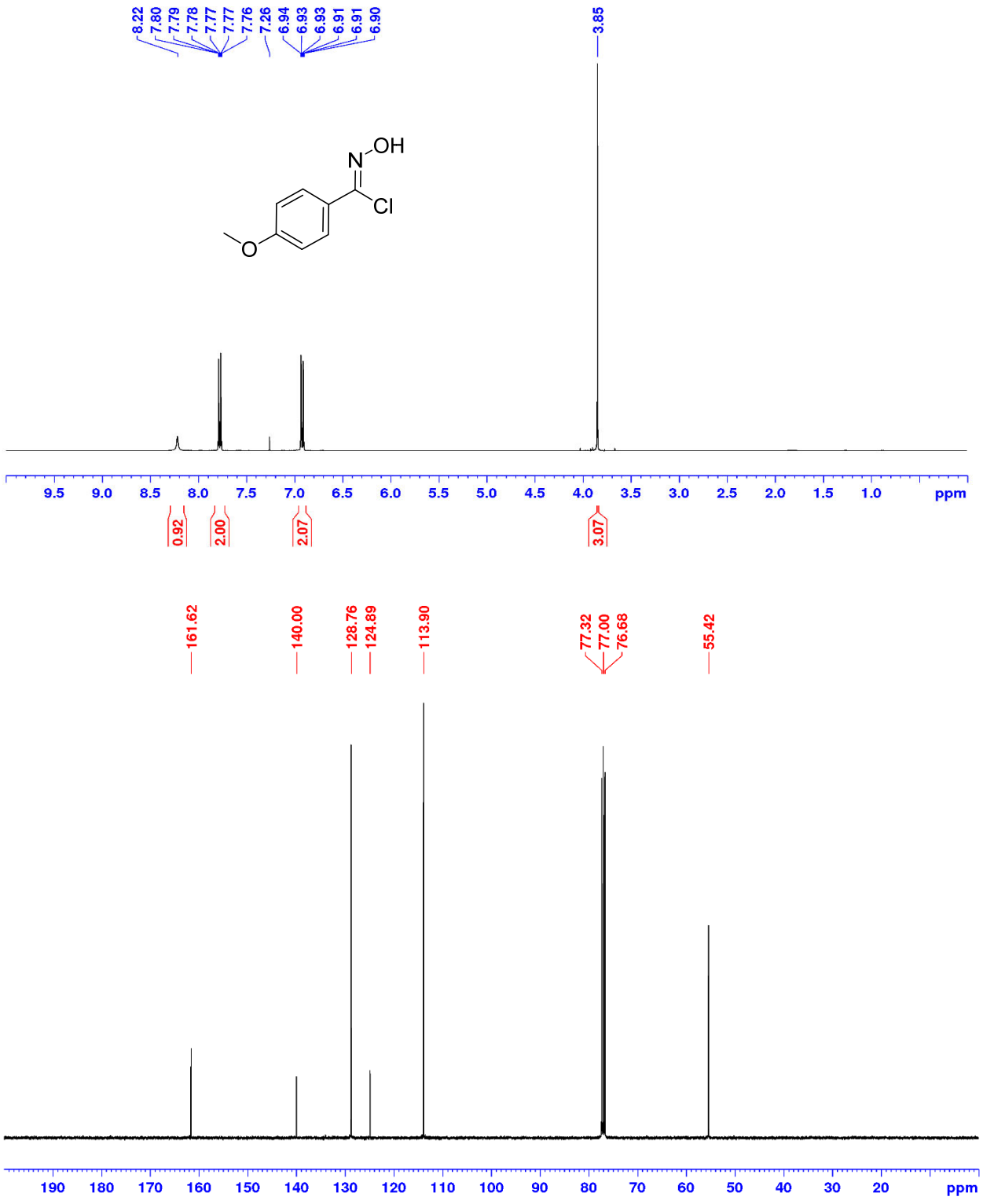


Figure S35. ^{1}H and ^{13}C NMR spectra of compound **3f** in $CDCl_3$

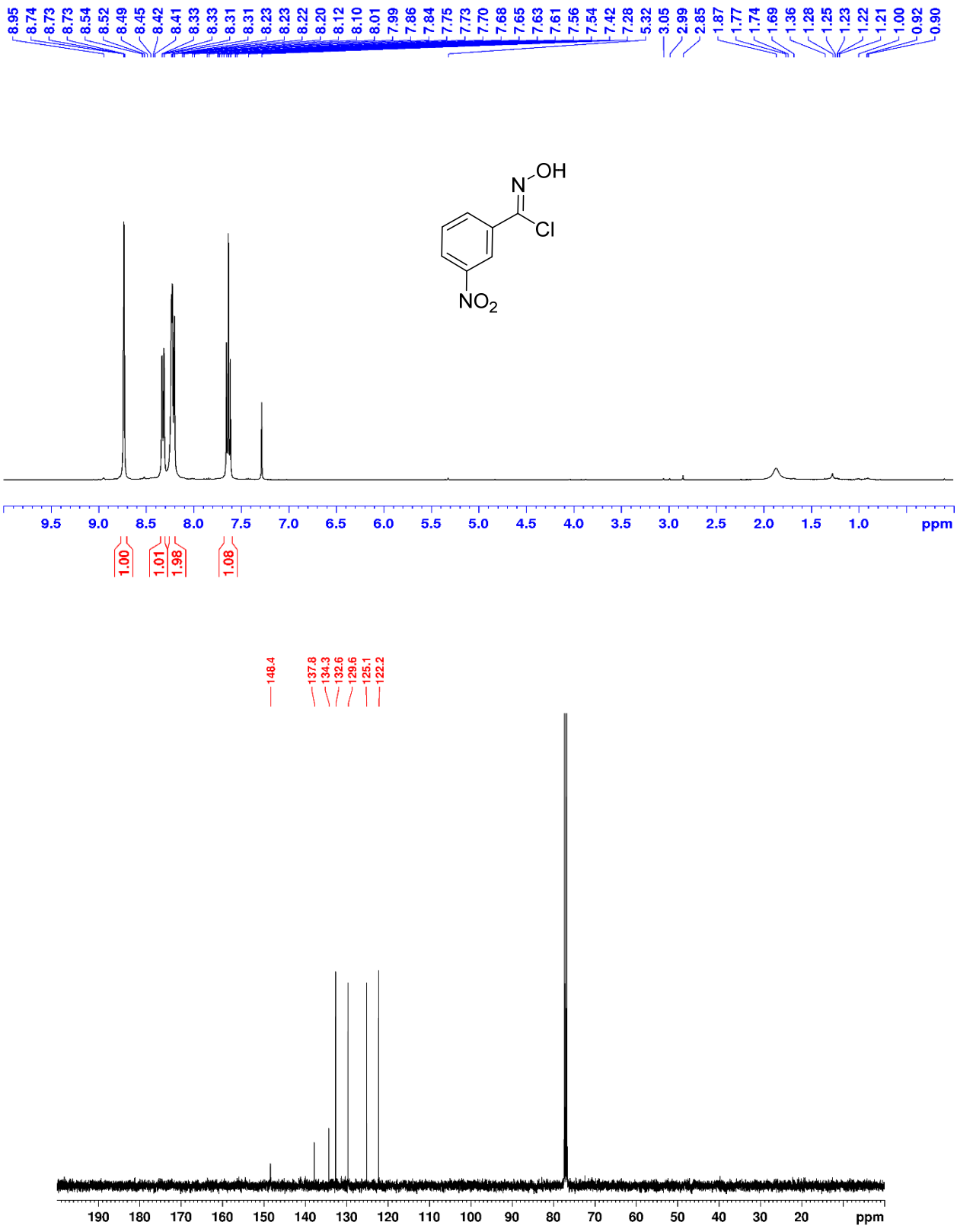


Figure S36. ^{1}H and ^{13}C NMR spectra of compound **3h** in $CDCl_3$

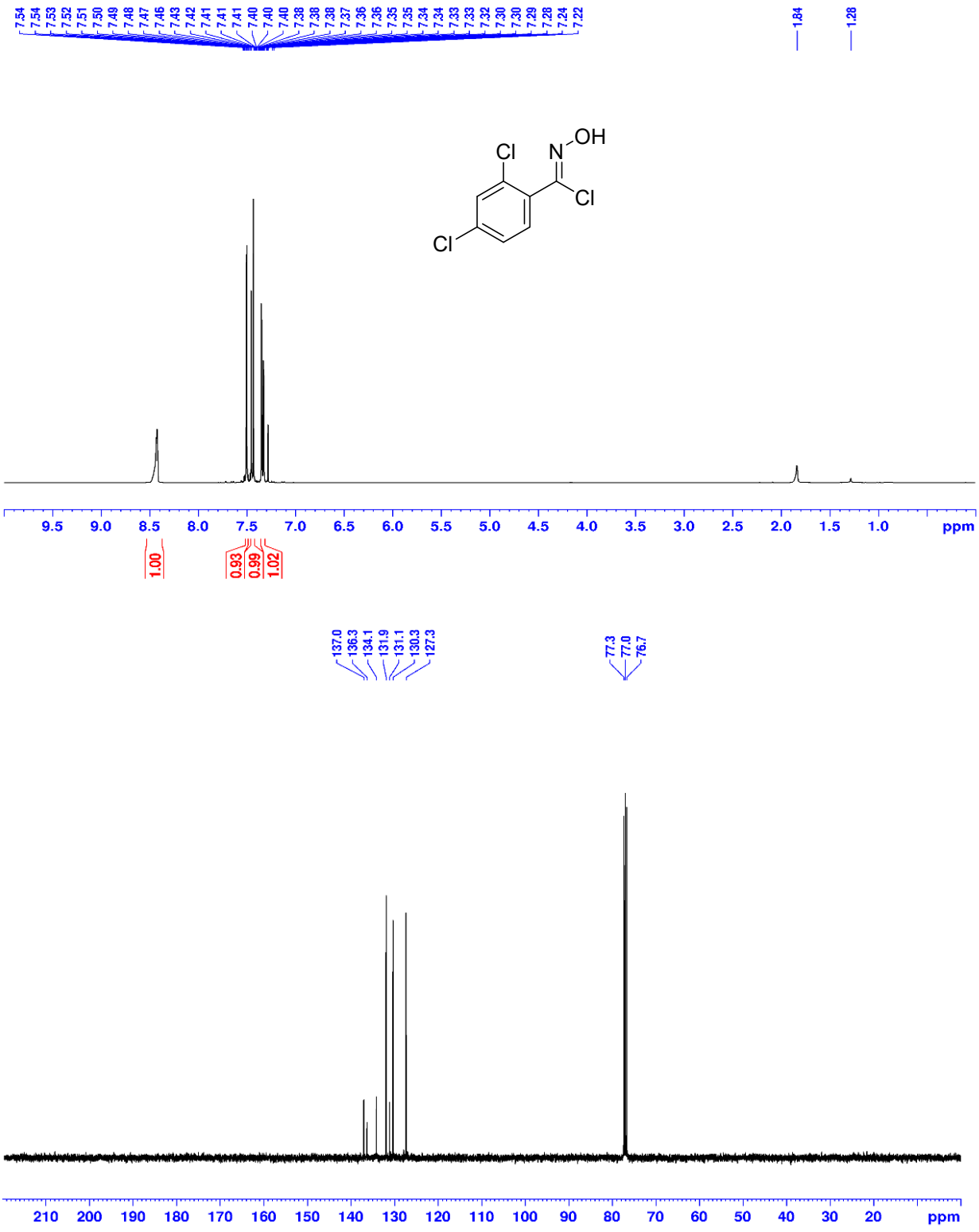


Figure S37. ^{1}H and ^{13}C NMR spectra of compound **3i** in $CDCl_3$

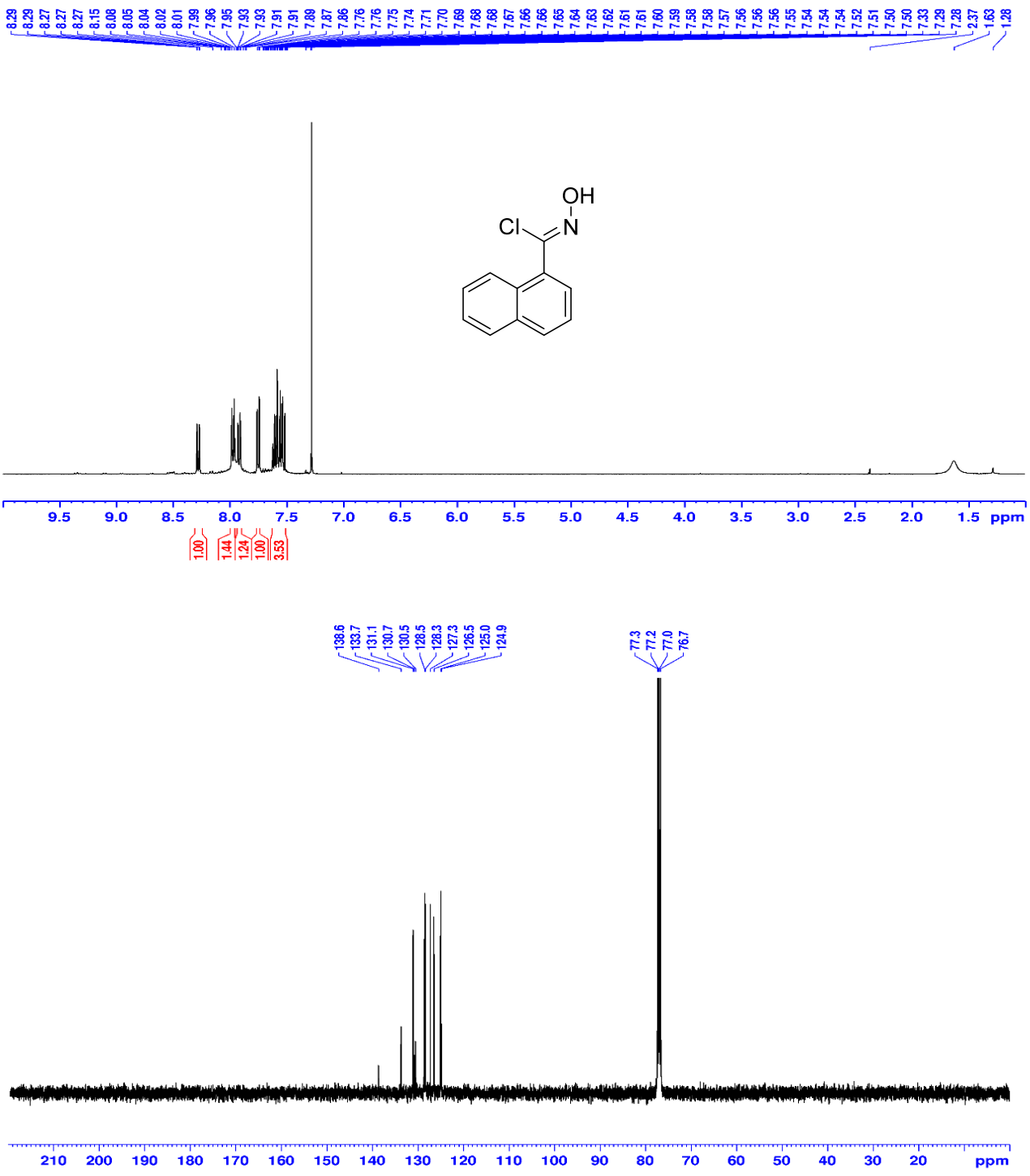


Figure S38. ^{1}H and ^{13}C NMR spectra of compound **3j** in $CDCl_3$

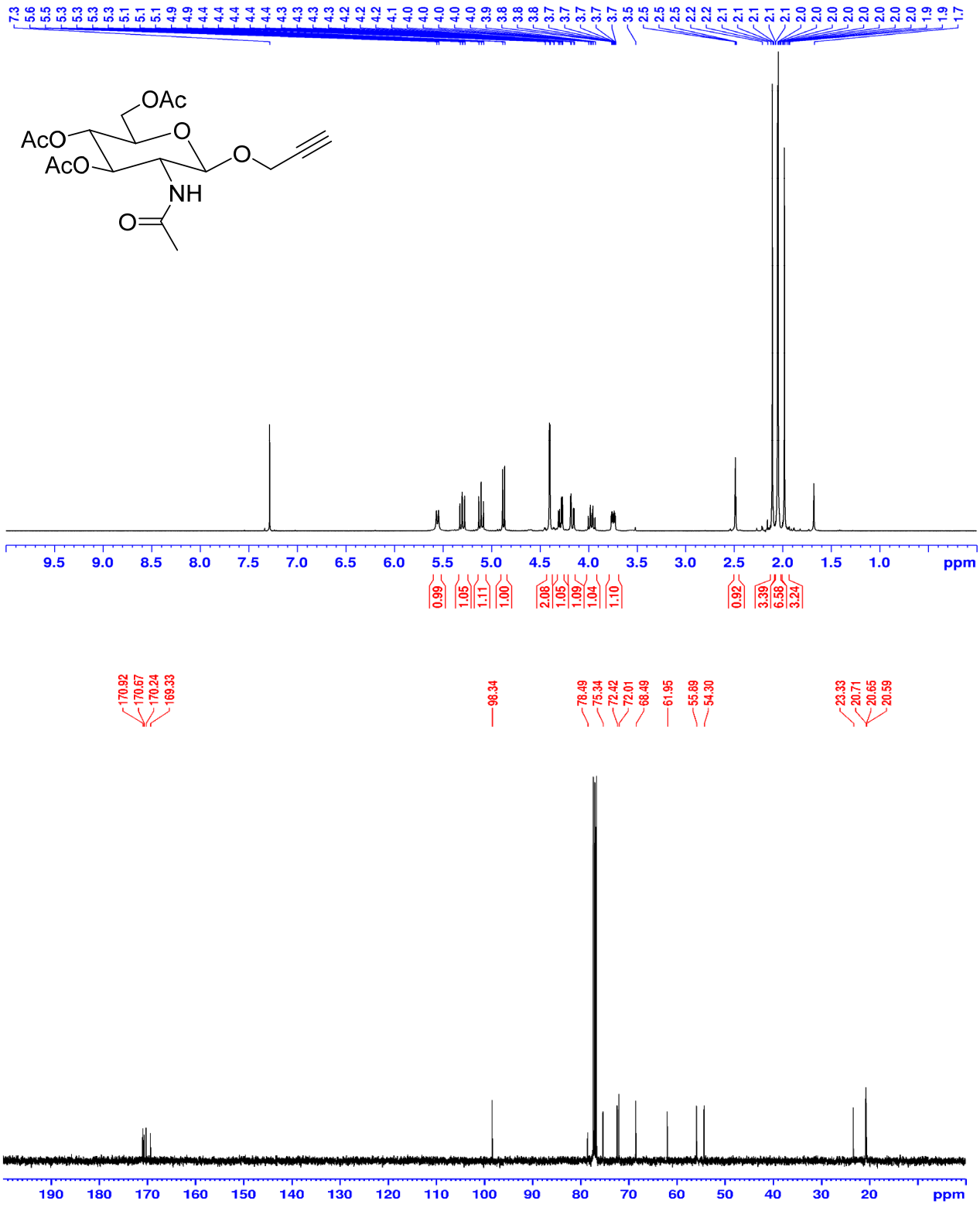


Figure S39. ^{1}H and ^{13}C NMR spectra of compound **4** in $CDCl_3$

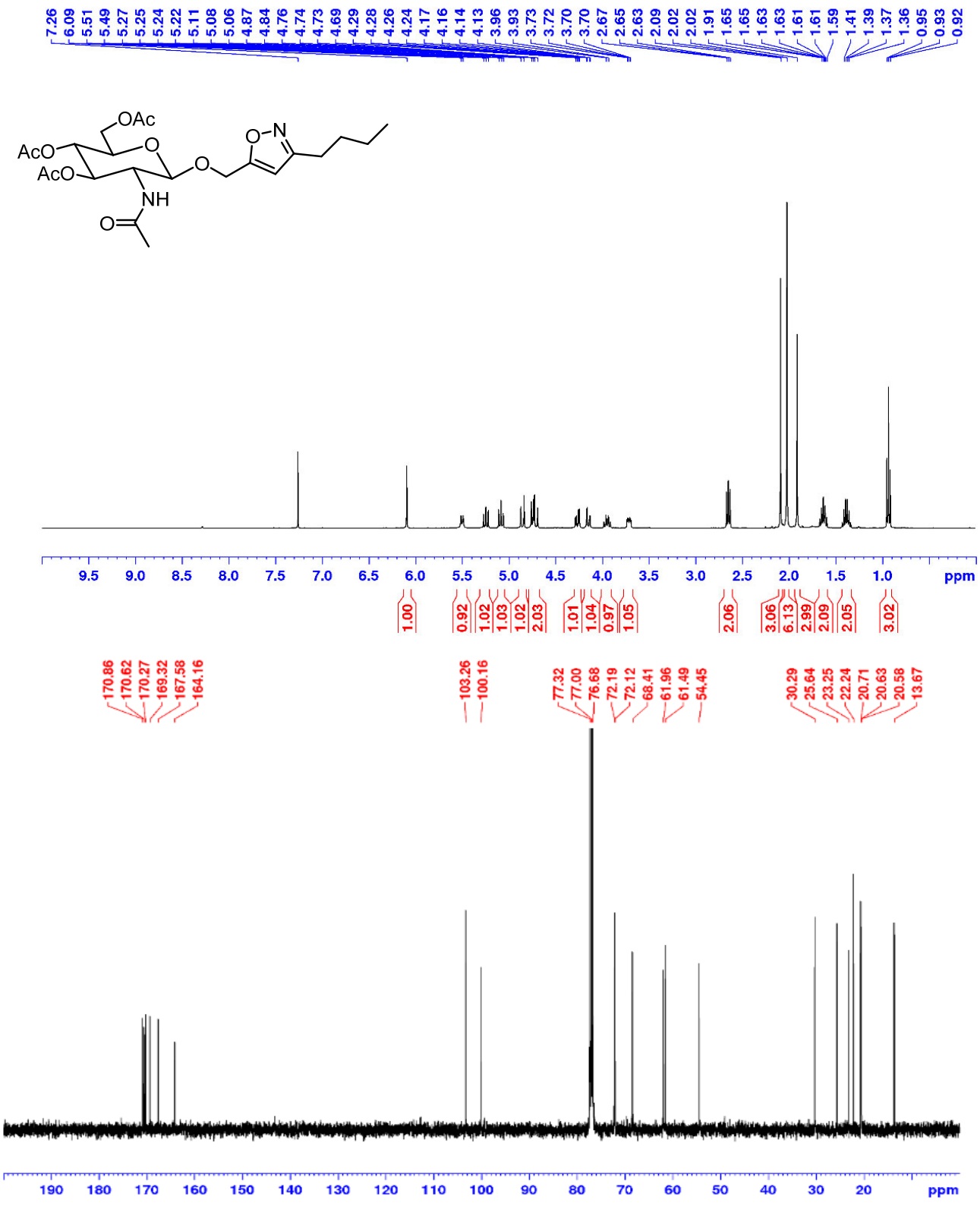


Figure 40. ^{1}H and ^{13}C NMR spectra of compound **5a** in $CDCl_3$

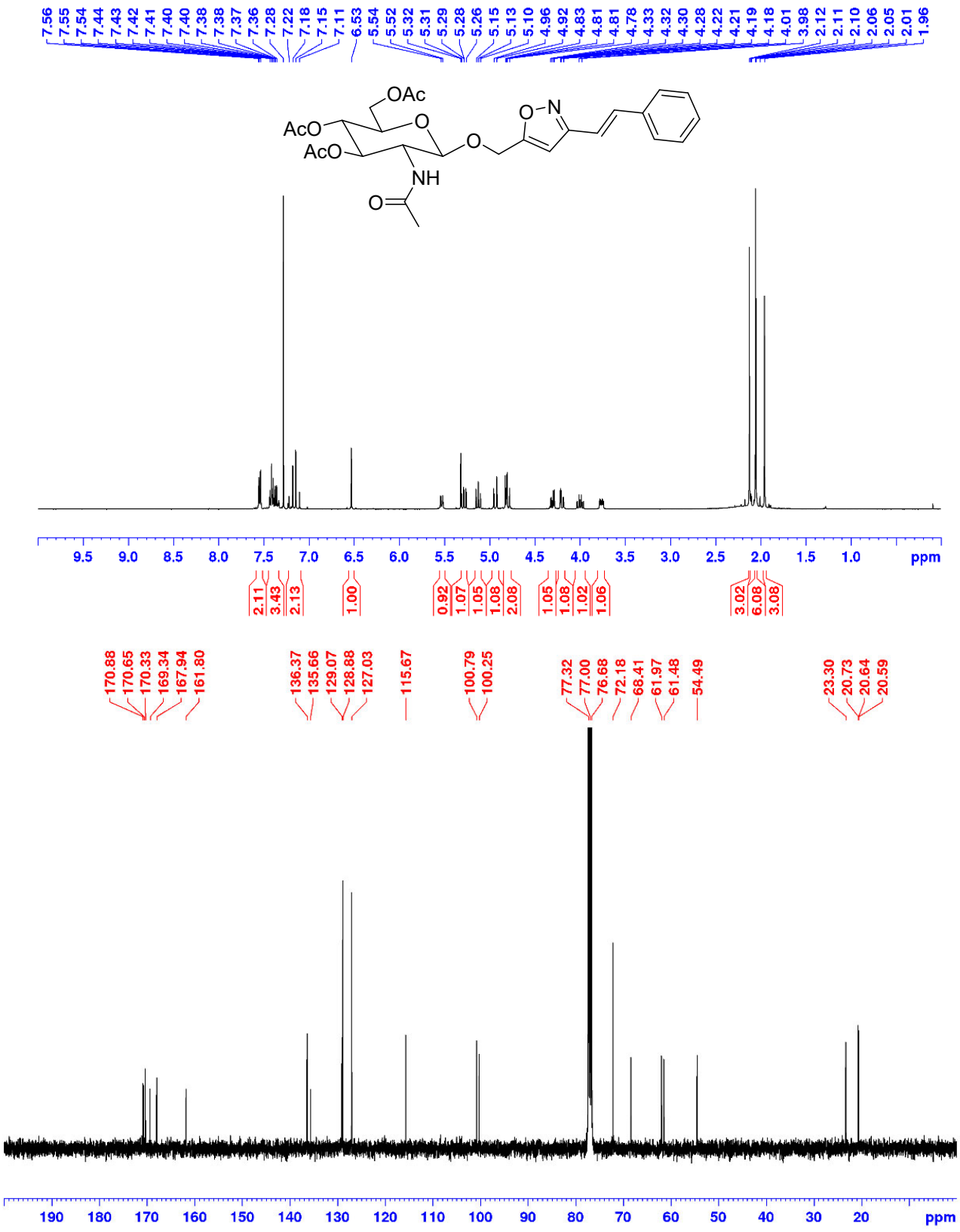


Figure S41. ^{1}H and ^{13}C NMR spectra of compound **5b** in $CDCl_3$

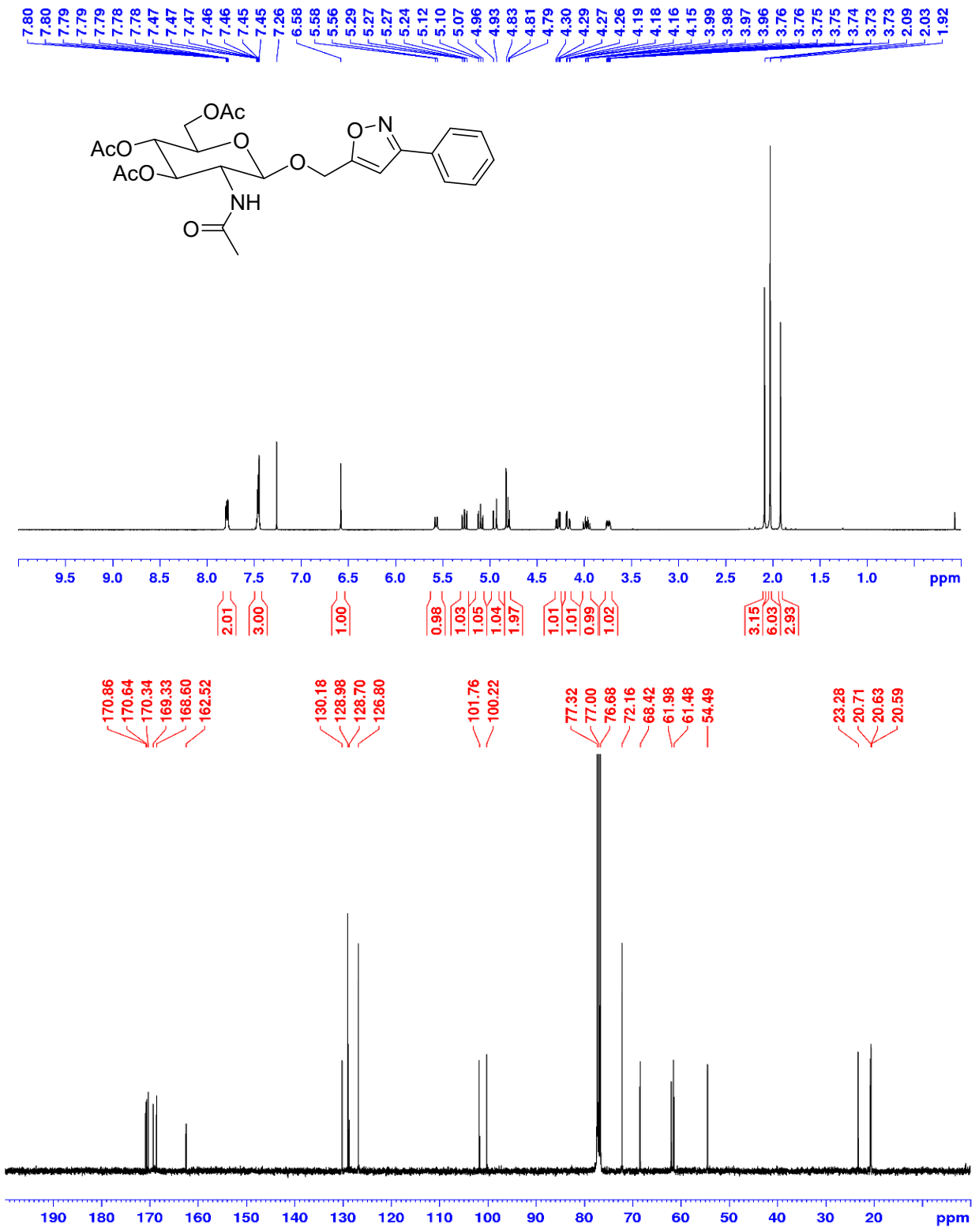


Figure S42. ^{1}H and ^{13}C NMR spectra of compound **5c** in $CDCl_3$

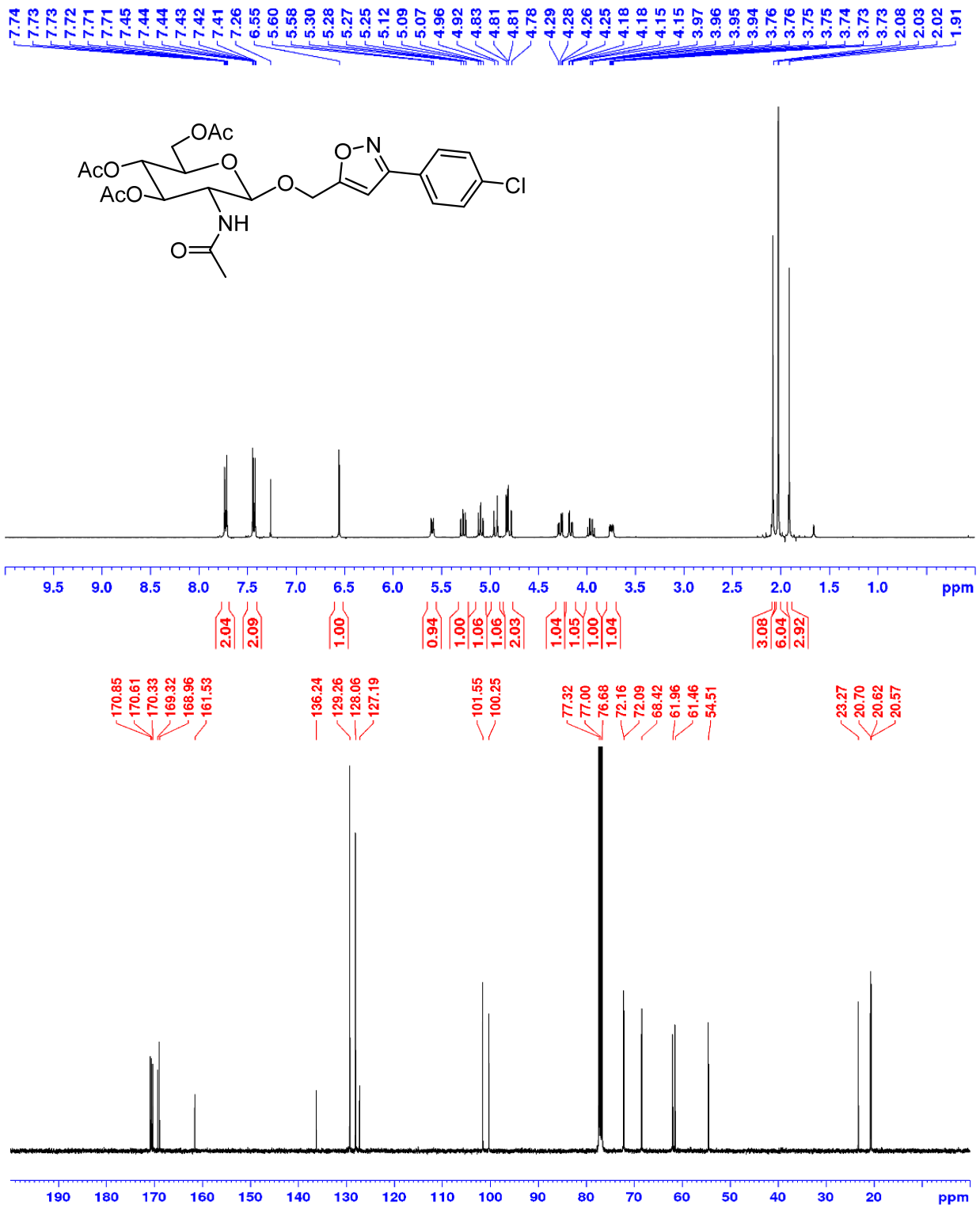


Figure S43. ^{1}H And ^{13}C NMR spectra of compound **5d** in $CDCl_3$

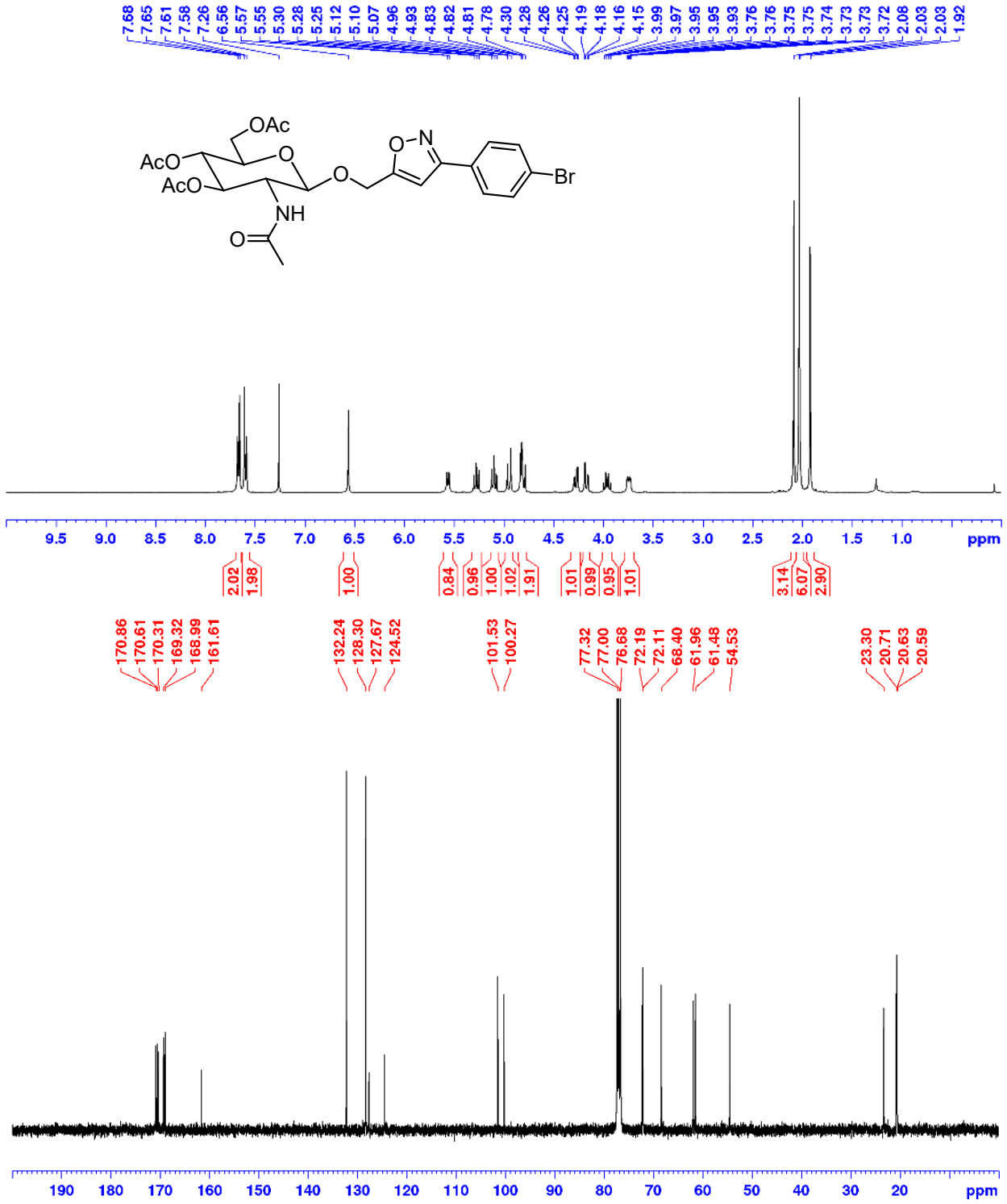


Figure S44. ^{1}H and ^{13}C NMR spectra of compound **5e** in $CDCl_3$

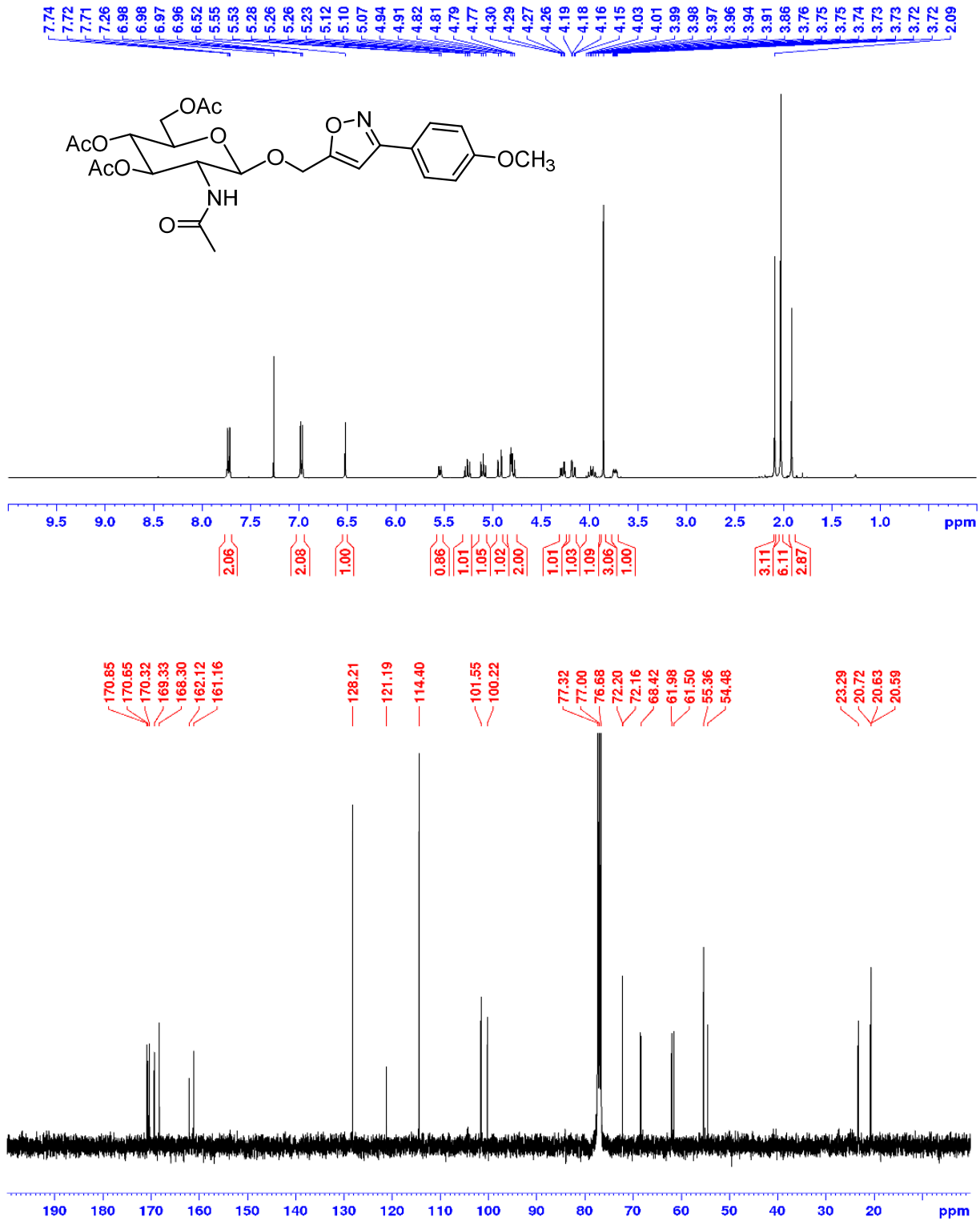
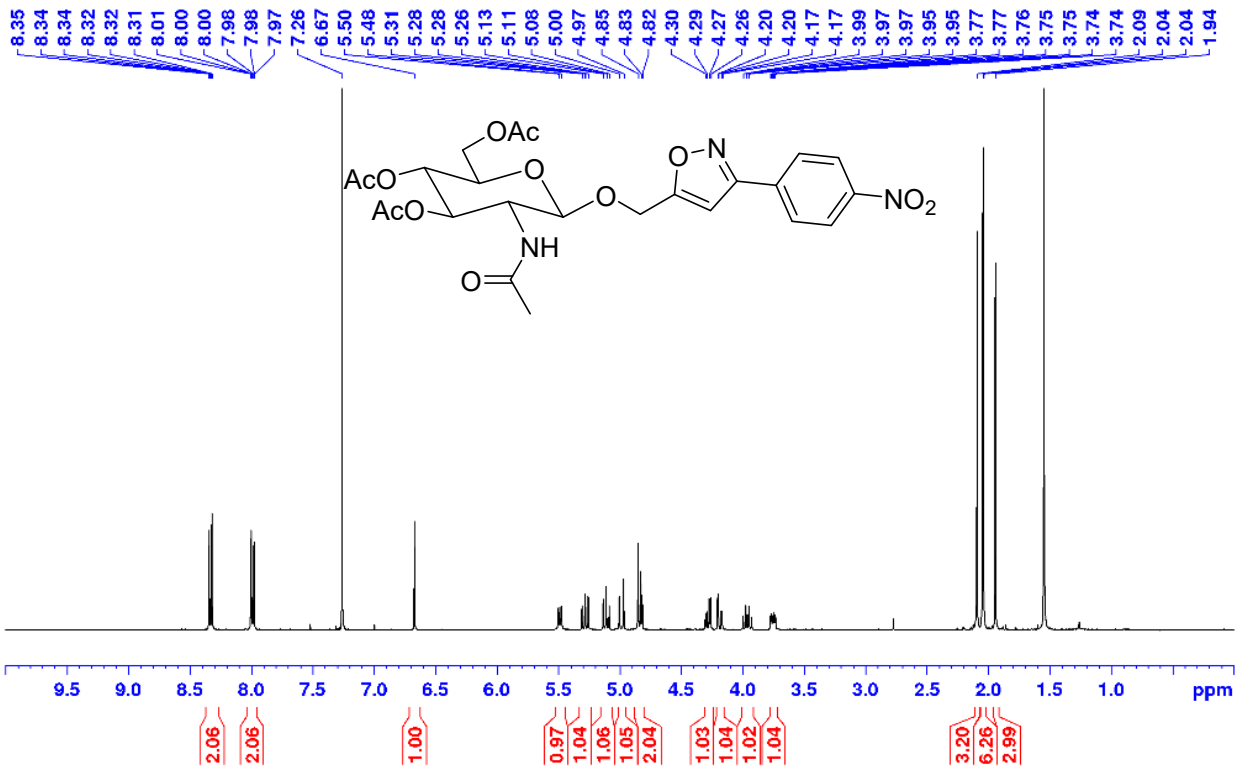


Figure S45. ^{1}H and ^{13}C NMR spectra of compound **5f** in $CDCl_3$


8.35 8.34 8.34 8.32 8.32 8.31 8.01 8.00 8.00 7.98 7.98 7.97 7.26 6.67 5.50 5.48 5.31 5.28 5.28 5.26 5.13 5.11 5.08 5.00 4.97 4.85 4.83 4.82 4.30 4.29 4.27 4.26 4.20 4.20 4.17 4.17 3.99 3.97 3.97 3.95 3.95 3.77 3.77 3.76 3.75 3.75 3.74 3.74 2.09 2.04 2.04 1.94
OAc
AcO
AcO
O
O
O-N
NH
O
NO2
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.06 2.06 1.00 0.97 1.04 1.06 1.05 2.04 1.03 1.04 1.02 1.04 3.20 6.26 2.99

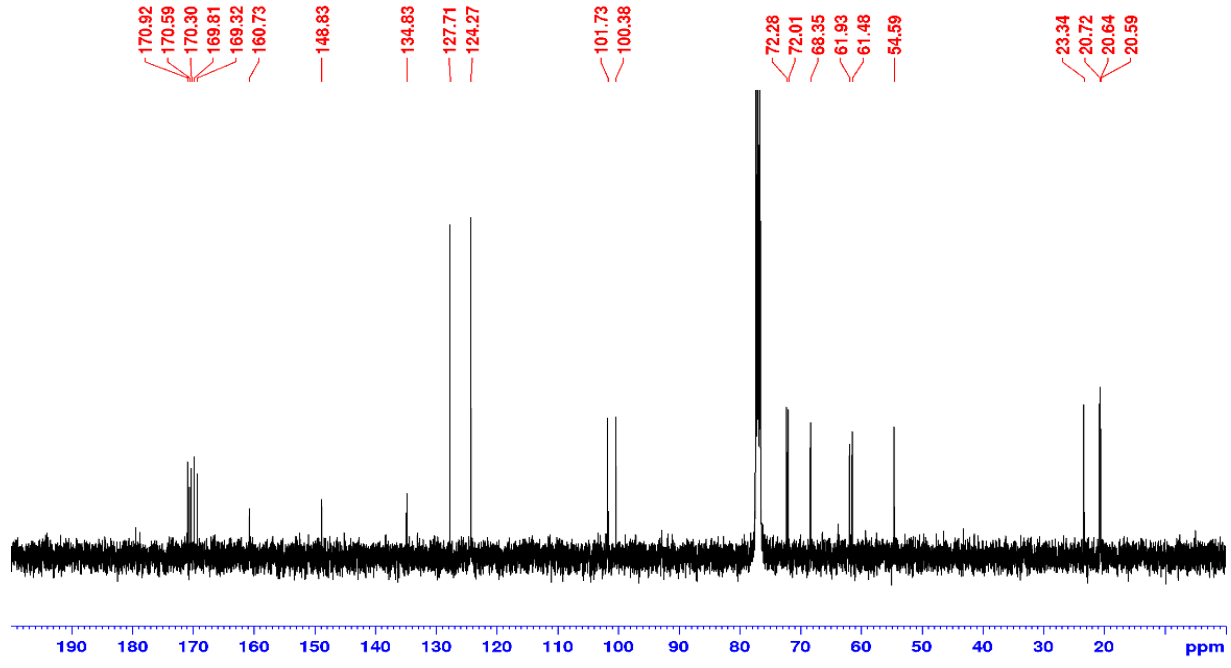

170.92 170.59 170.30 169.81 169.32 160.73 148.83 134.83 127.71 124.27 101.73 100.38 72.28 72.01 68.35 61.93 61.48 54.59 23.34 20.72 20.64 20.59
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

Figure S46. ^{1}H and ^{13}C NMR spectra of compound **5g** in $CDCl_3$

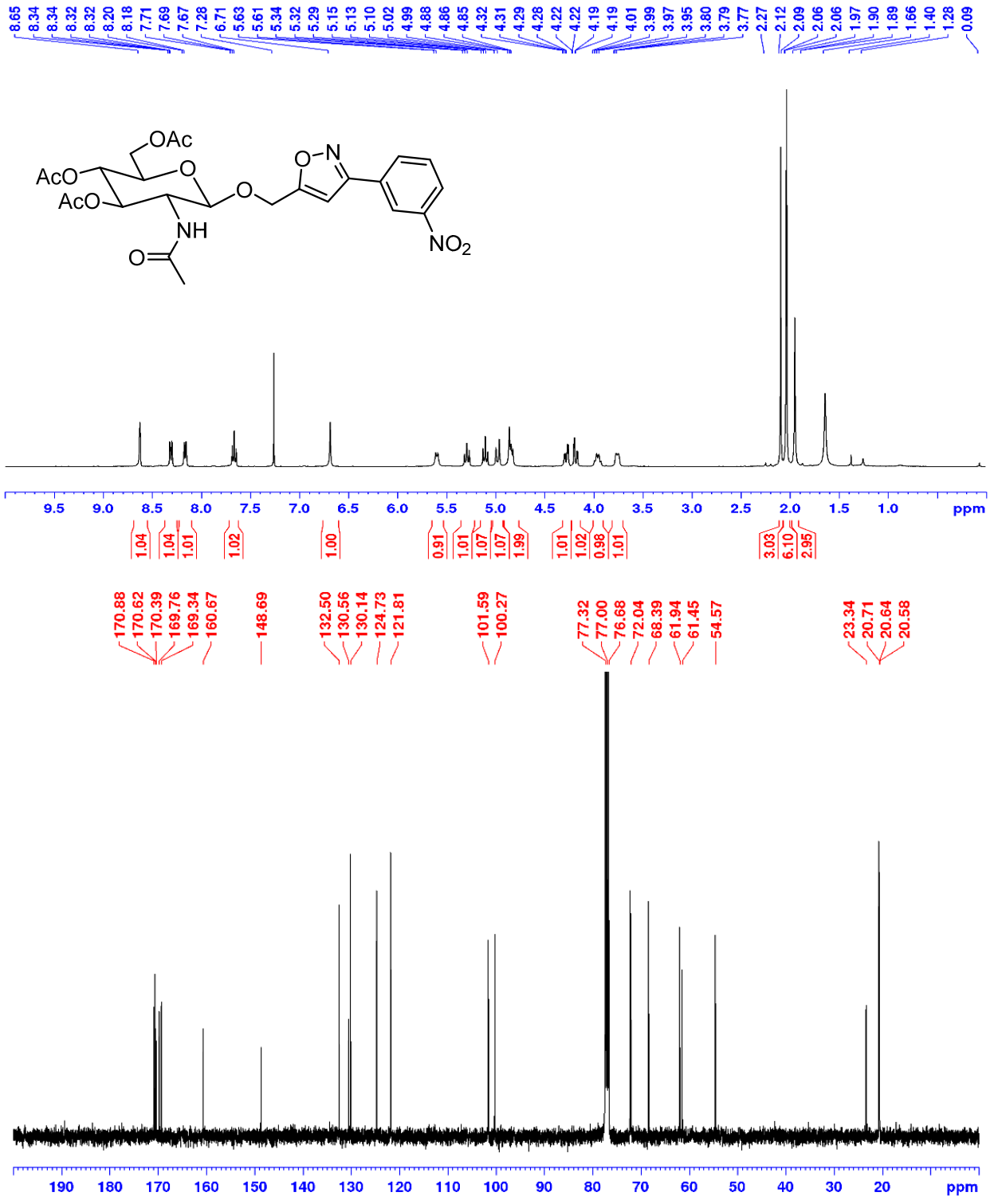


Figure S47. ^{1}H and ^{13}C NMR spectra of compound **5h** in $CDCl_3$

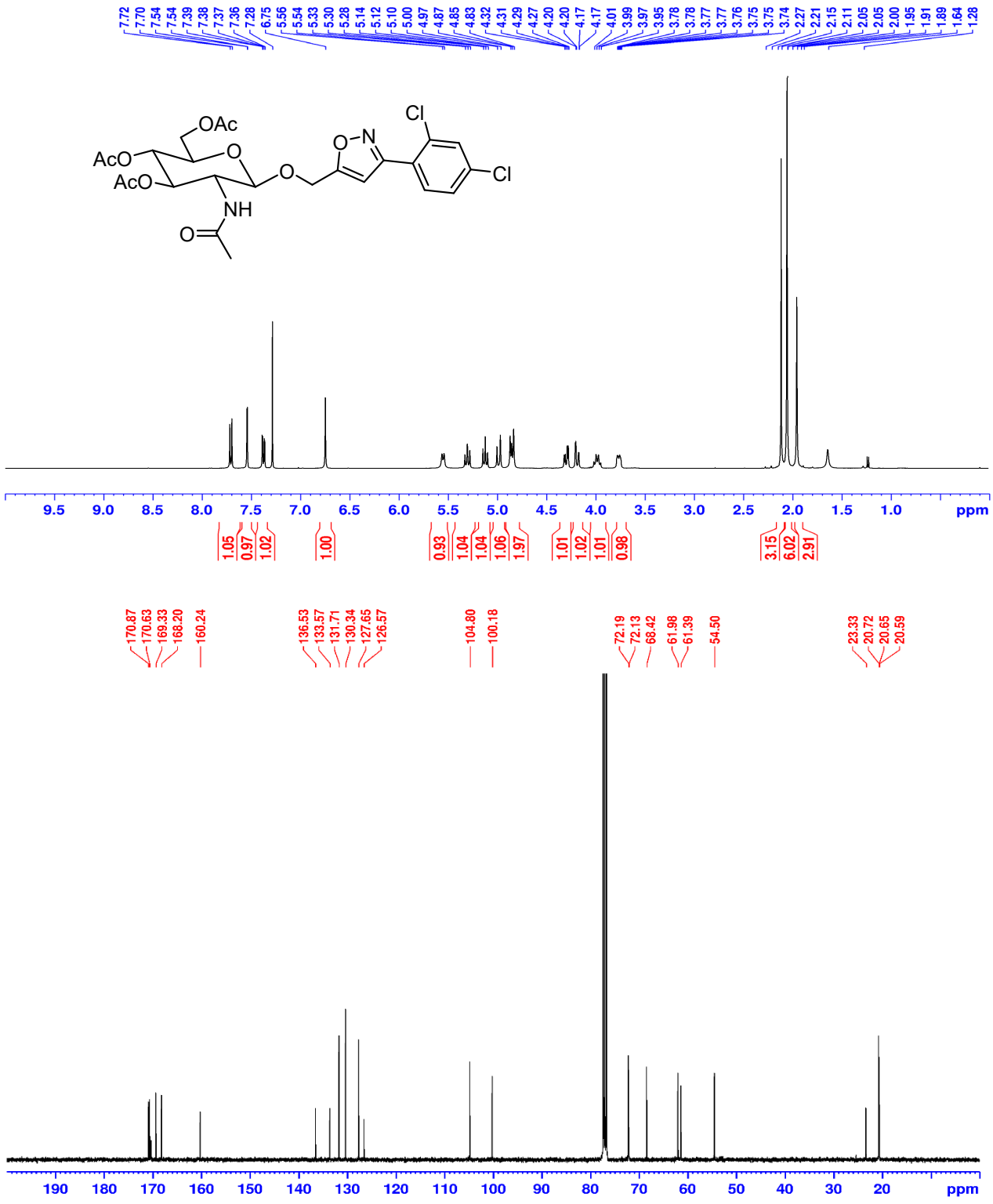


Figure S48. ^{1}H and ^{13}C NMR spectra of compound **5i** in $CDCl_3$

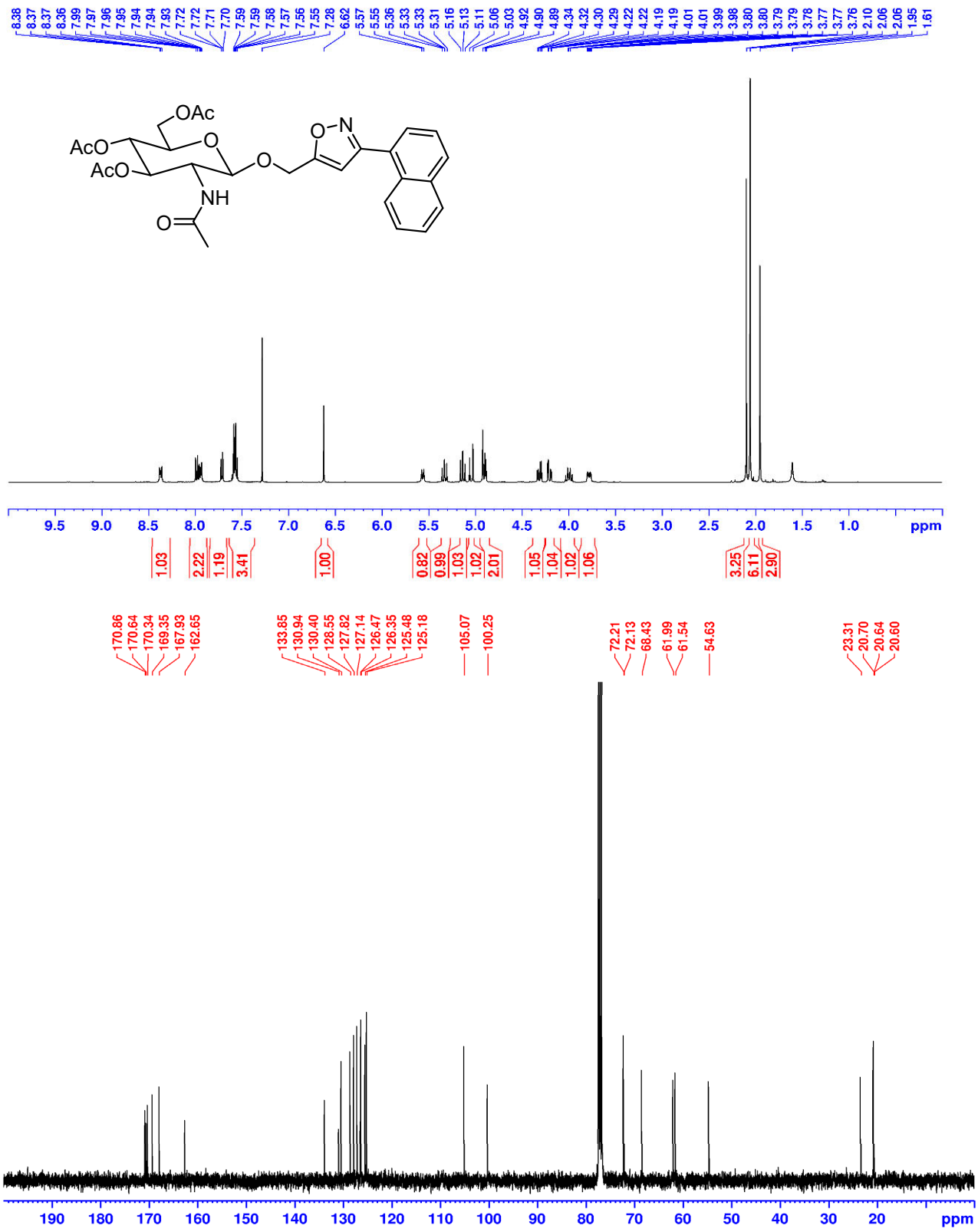


Figure S49. ^{1}H and ^{13}C NMR spectra of compound **5j** in $CDCl_3$

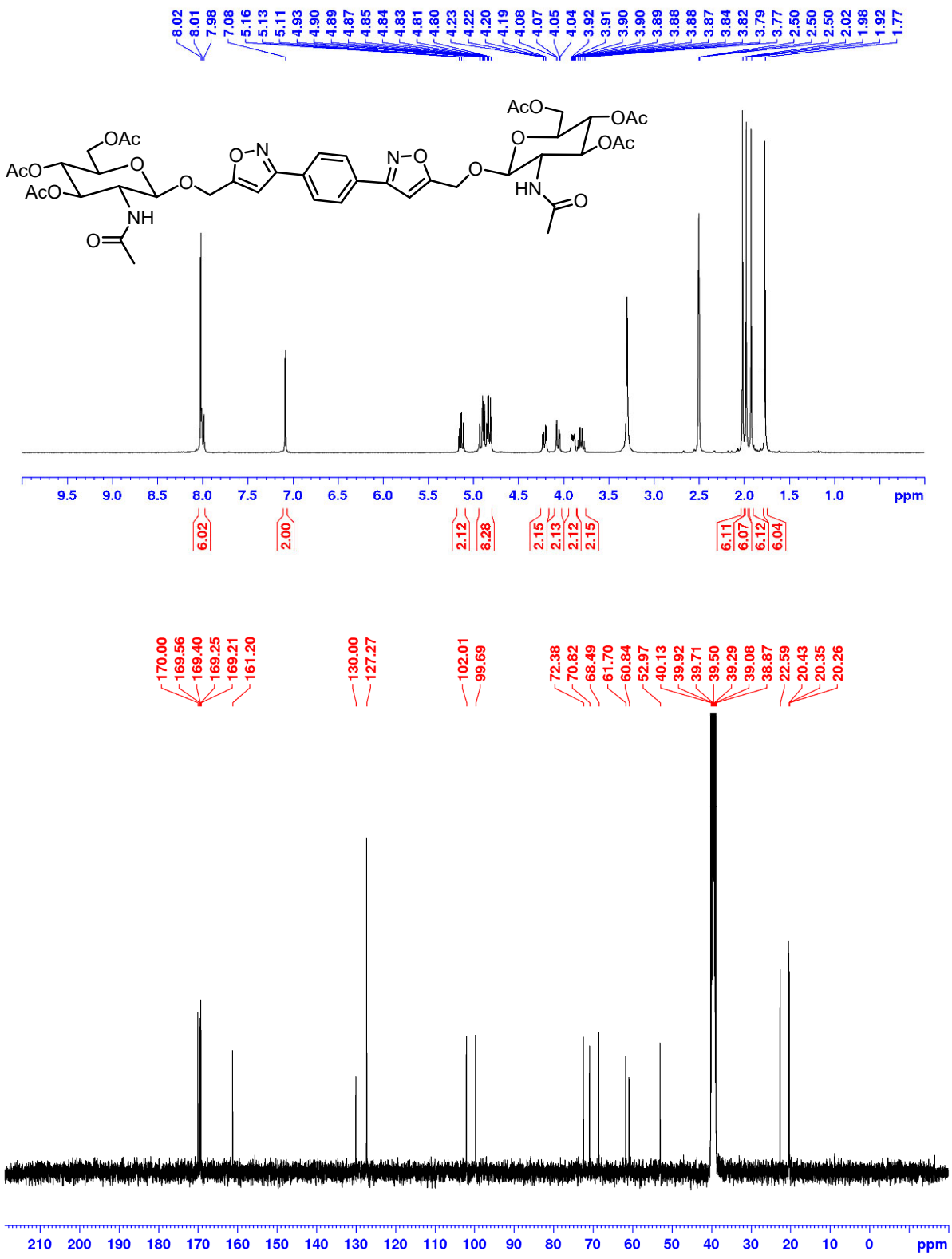


Figure S50. ^{1}H and ^{13}C NMR spectra of compound **5k** in d_6-DMSO

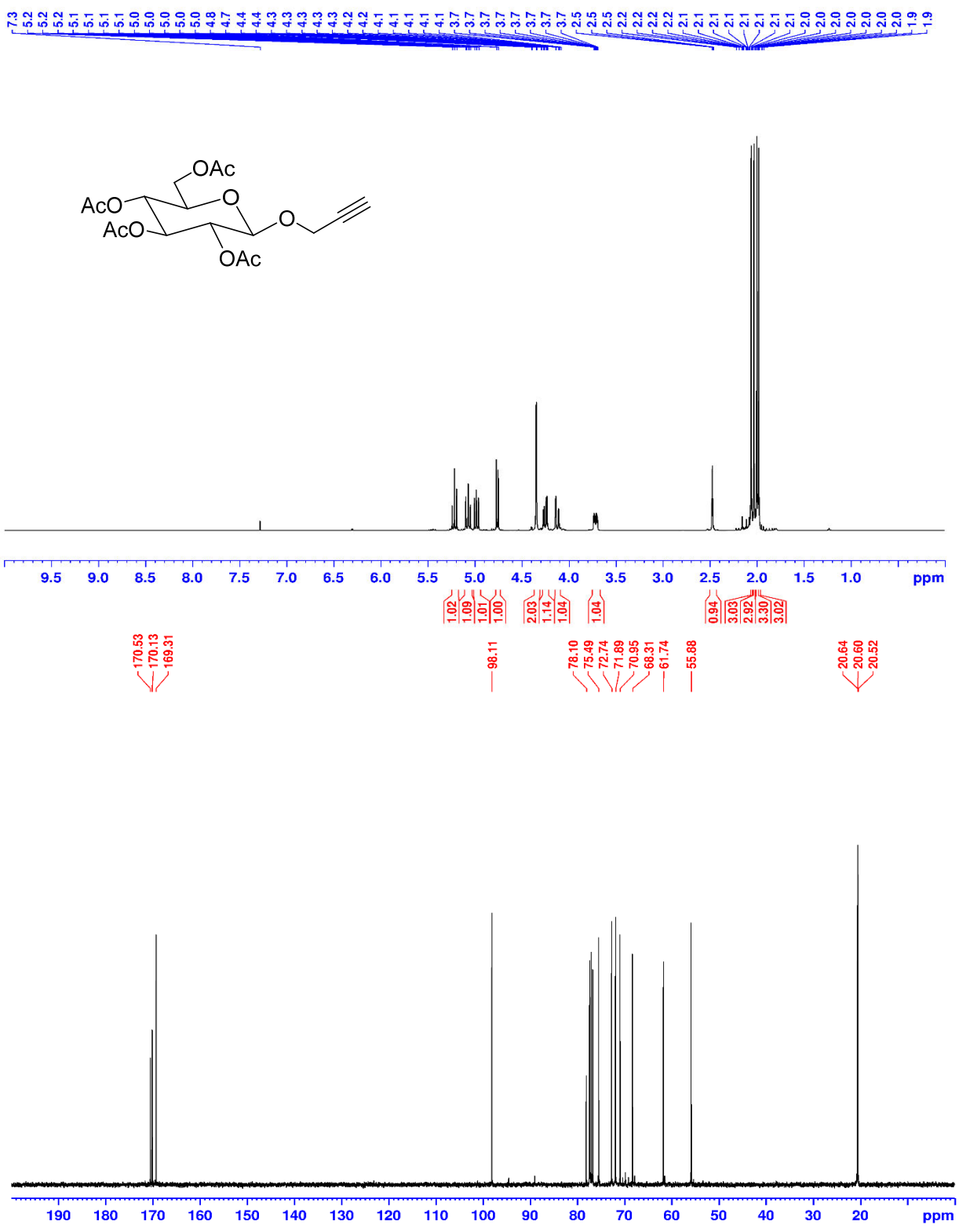


Figure S51. ^{1}H and ^{13}C NMR spectra of compound **6** in $CDCl_3$

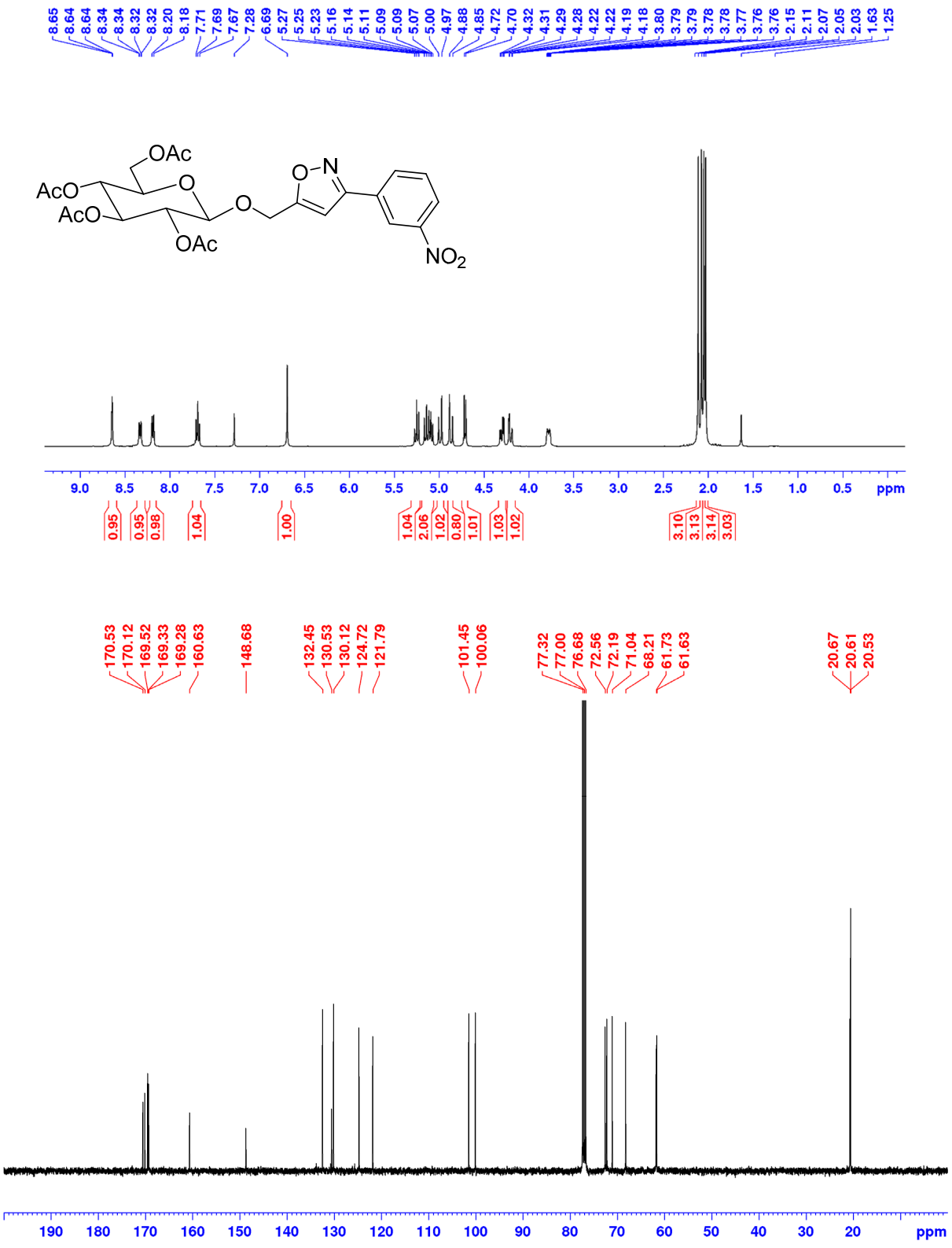


Figure S52. ^{1}H and ^{13}C NMR spectra of compound **7h** in $CDCl_3$

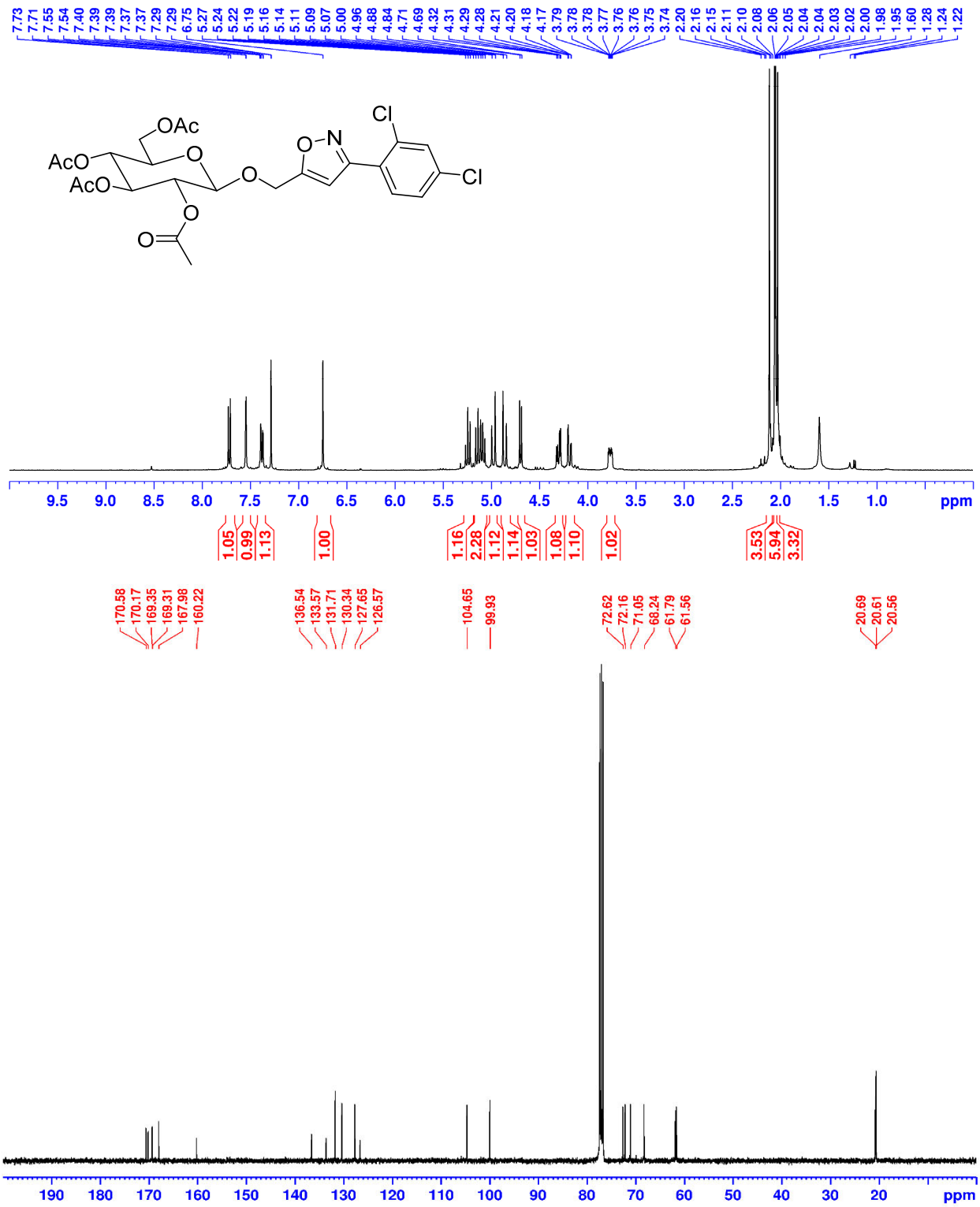


Figure S53. ^{1}H and ^{13}C NMR spectra of compound **7i** in $CDCl_3$

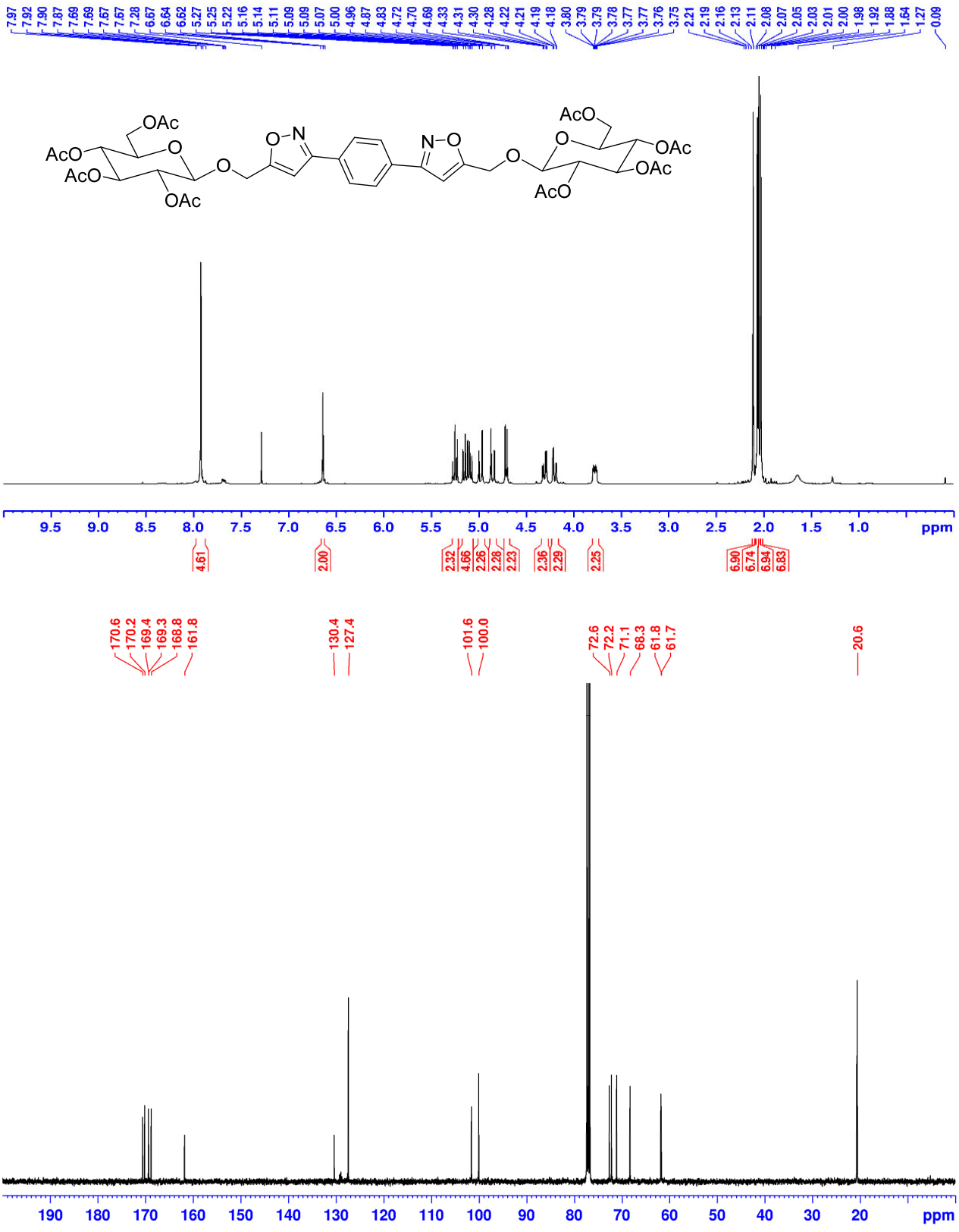


Figure S54. ^{1}H and ^{13}C NMR spectra of compound **7k** in $CDCl_3$

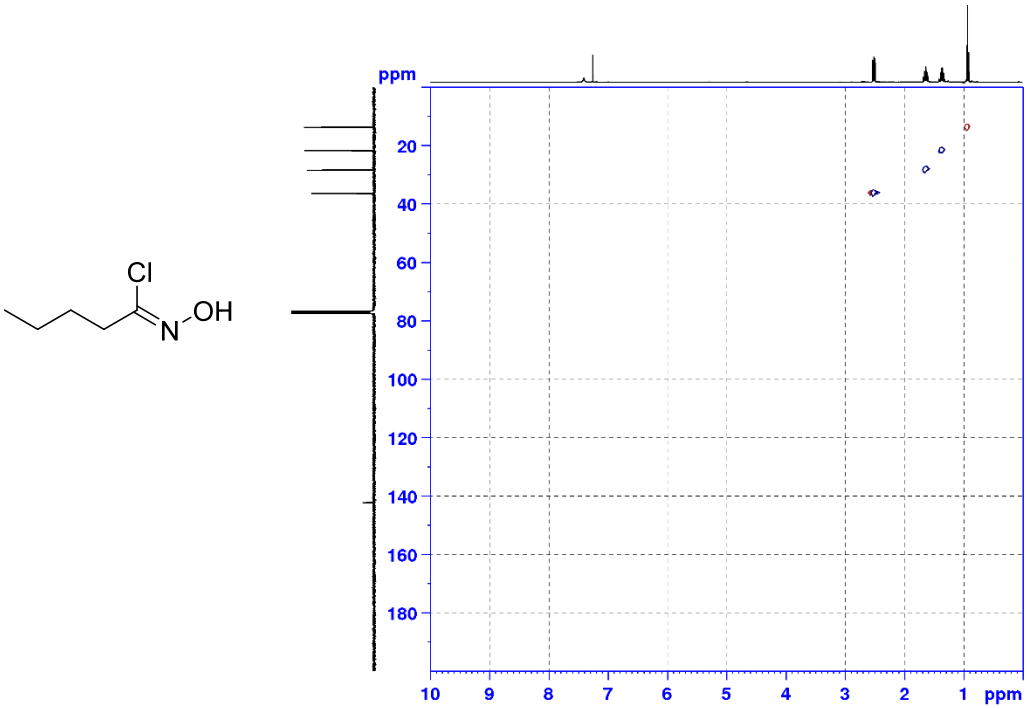


Figure S55. 2D HSQC NMR spectrum of compound **3a** in $CDCl_3$

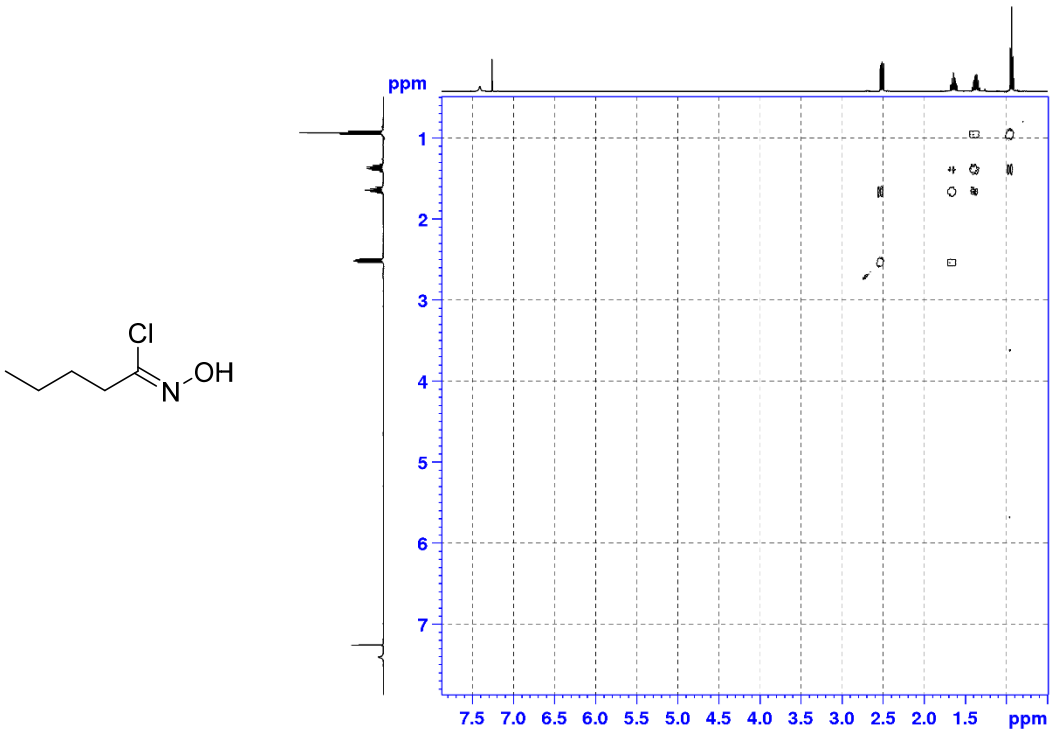


Figure S56. 2D COSY NMR spectrum of compound **3a** in $CDCl_3$

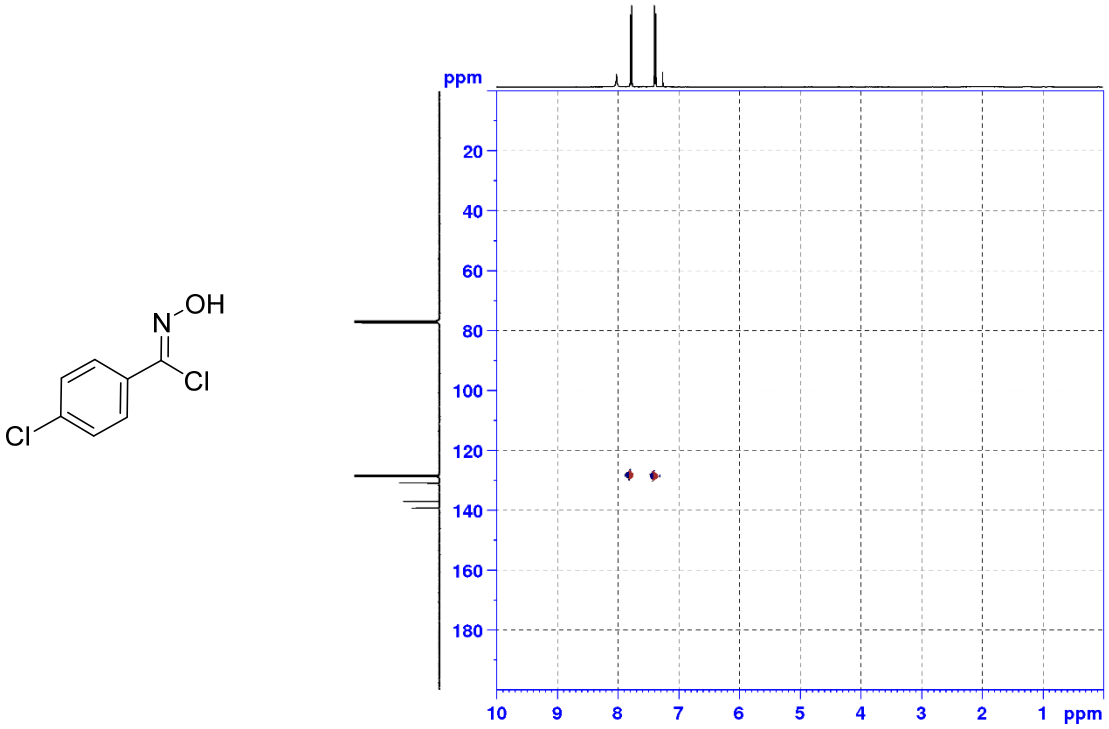


Figure S57. 2D HSQC NMR spectrum of compound **3d** in $CDCl_3$

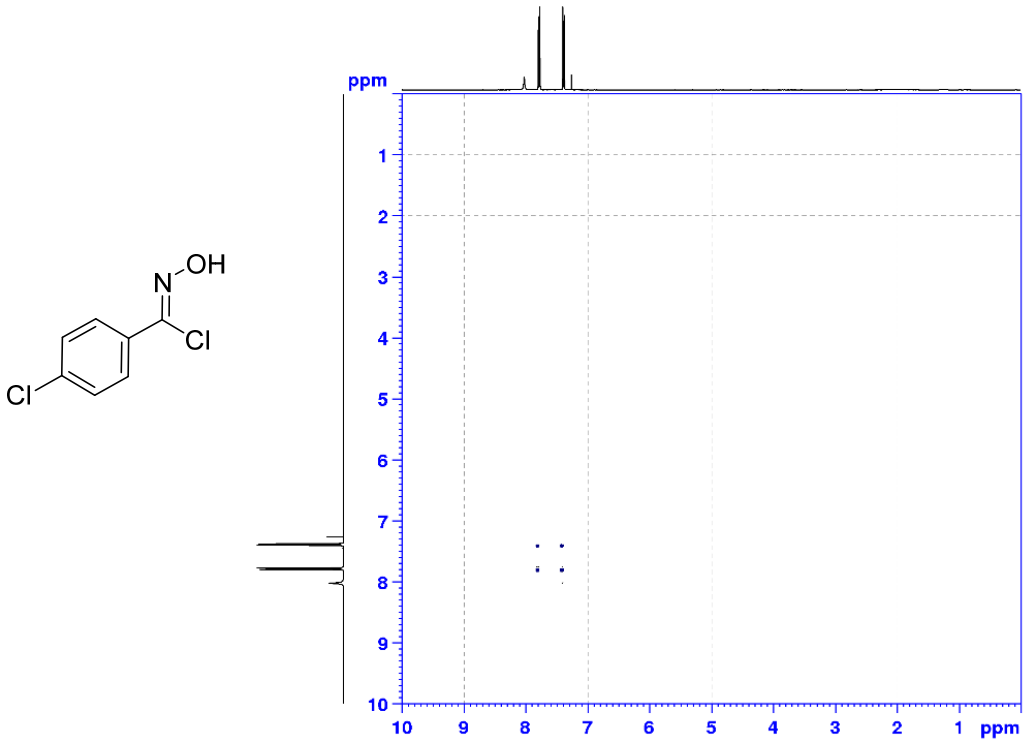


Figure S58. 2D COSY NMR spectrum of compound **3d** in $CDCl_3$

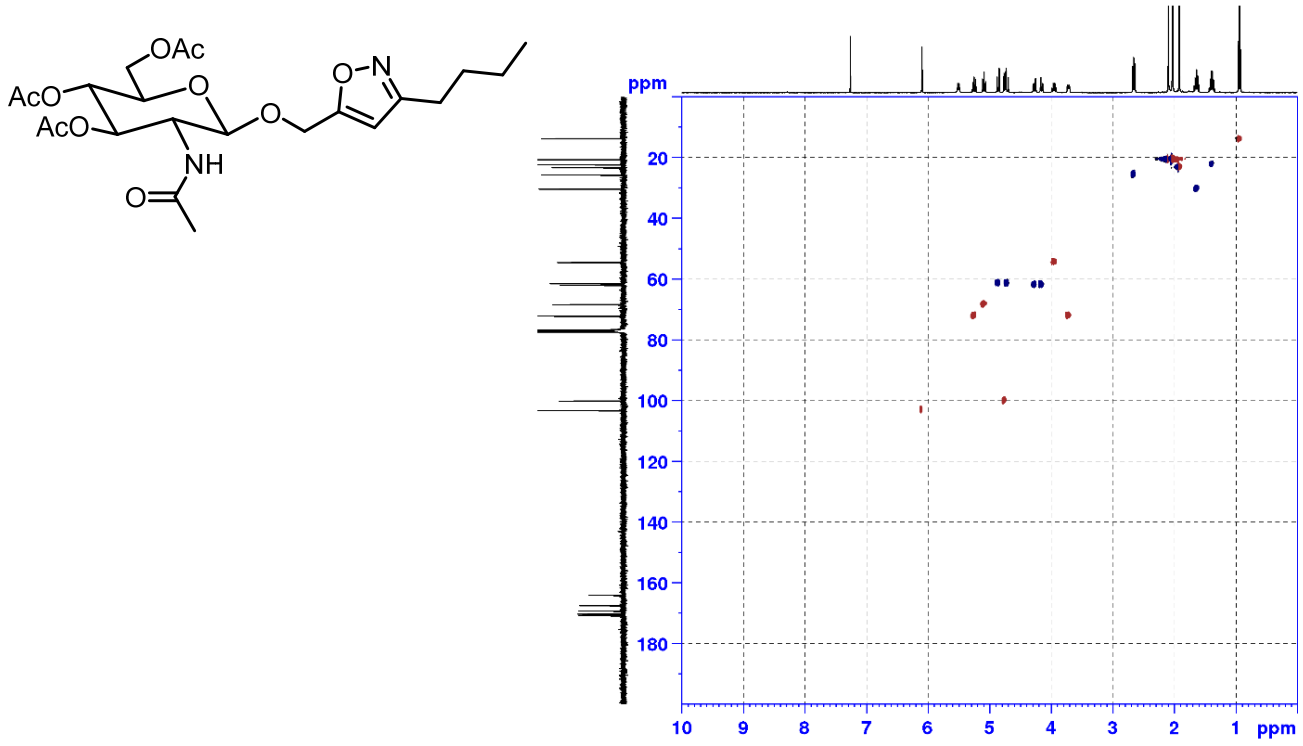


Figure S59. 2D HSQC NMR spectrum of compound **5a** in $CDCl_3$

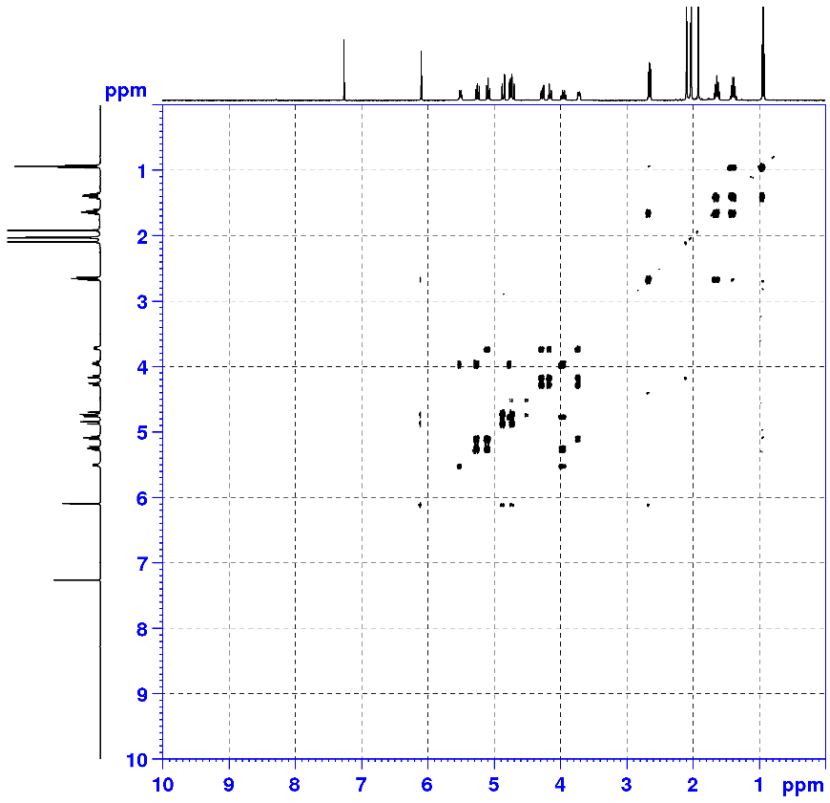
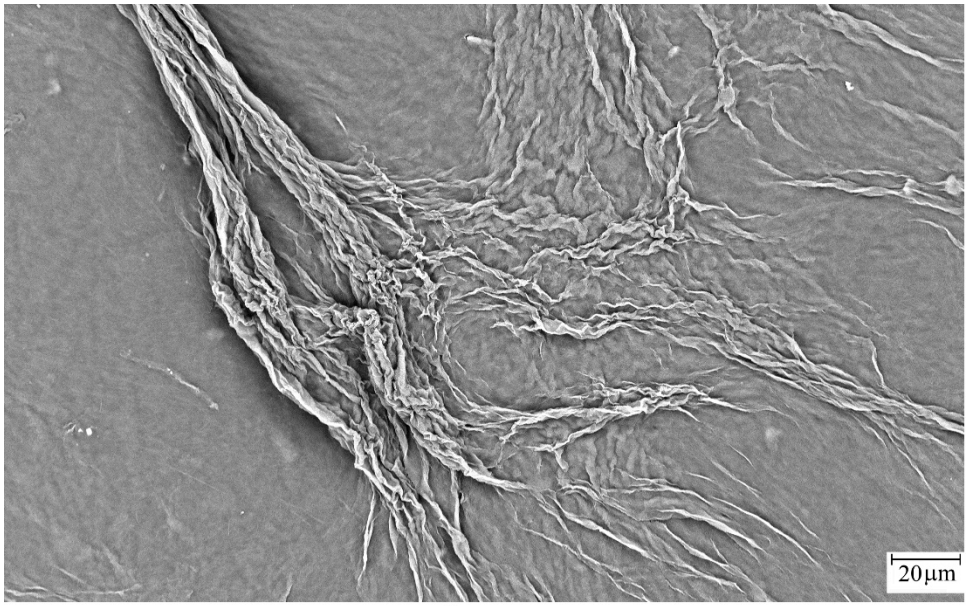
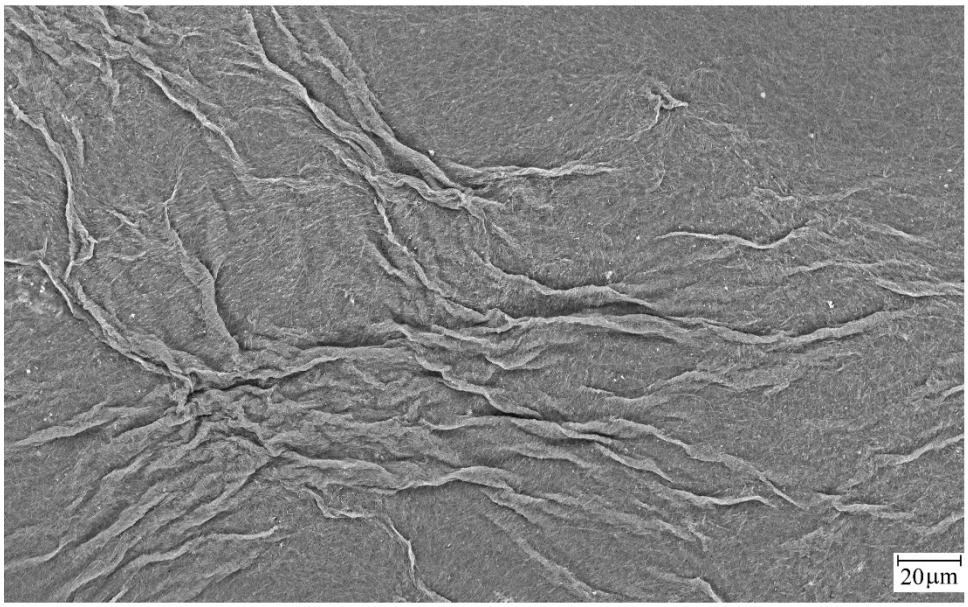


Figure S60. 2D COSY NMR spectrum of compound **5a** in $CDCl_3$



a



b

Figure S61. Scanning electronic micrographs of the hydrogels formed by: a) Compound **5h** at 2.0 mg/mL; b) Compound **5d** at 1.1 mg/mL with $Zn(OAc)_2$.

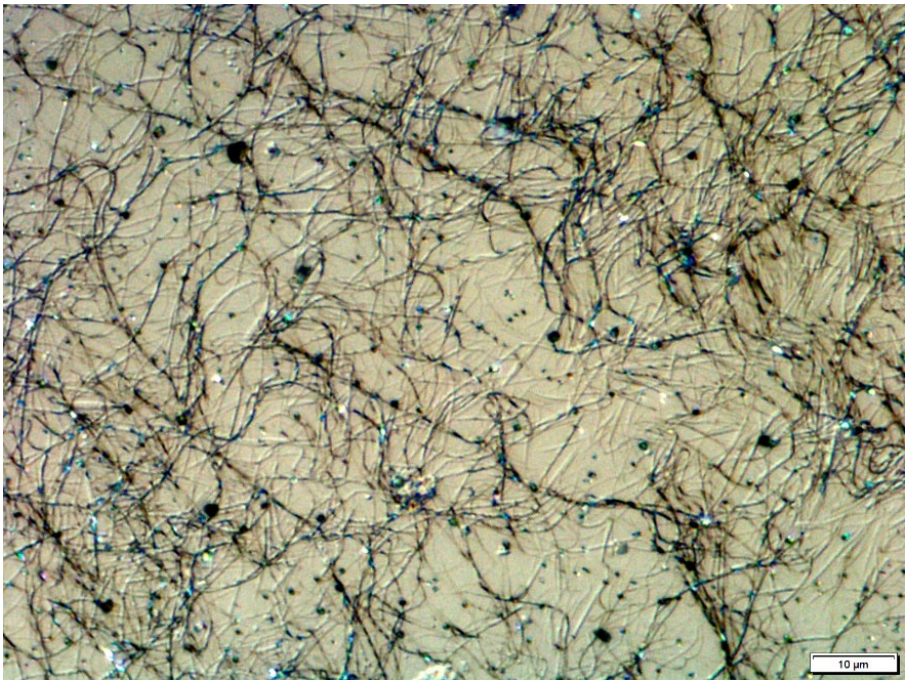


Figure S62. An optical micrograph of the gel formed by compound **5d** in water at 1.1 mg/mL with $NiCl_2$.

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